STUDIES ON ACENAPHTHENE AND ITS OXIDATION PRODUCTS

By

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C O N T E N T S

GENERAL INTRODUCTION.

The Discovery and Synthesis of Acenaphthene.

In 1867 Marcelin Berthelot published a long memoir embracing several parts under the general title "Des Carbures Pyrogénés" (Annales de Chimie et de Physique, 4^{e} series, t XII, 5-96, 122-243). The pyrogenic syntheses of styrolene, naphthalene and anthracene are described and also that of benzene from acetylene. The last-mentioned reaction taken in conjunction with Berthelot's synthesis of acetylene from its elements in the electric arc constitutes the well-known complete synthesis of benzene. The synthesis of toluene and other coal-tar hydrocarbons follows, with a discussion of the thermodynamical considerations involved. Various other related studies are

communicated concluding with a paper, "Sur divers carbures contenus dans le goudron de huile". It is here that mention is first made of acenaphthene. Berthelot says, "Je désigne sous ce nom un nouveau carbure que j'ai découverte dans le goudron de huile parmi les produits de volatilité intermediare entre la naphthaline et l'anthracene". It was his pyrogenic syntheses that led him to its identification, for he also obtained it from naphthalene and ethylene.

Quite a number of the more obvious properties and reactions of acenaphthene are described in this memoir while less detailed accounts were published in other journals. (Ann. Suppt., 1867-68, 5, 372; Compt. rend., 1867, LXV, 465, 507)

Berthelot gives as the empirical formula of acenaphthene $C_{24}H_{10}$. At such a late date it is surprising to find the atomic weight of carbon regarded as 6, general adoption of Avogadro's hypothesis (1811) having followed Cannizzarro's exposition in 1858. In this connection a quotation from the Berthelot Memorial Lecture delivered by Dixon in 1911 (Chem. Soc. Mem. Lects., vol. ii) is of interest. "I ventured just now to compare Berthelot's mode of thought with Dalton's [in tendency to allow theoretical conception to outstrip experiment]. May we extend the parallelism further and say that the intensity of conception in the mind of each was sometimes too strong to yield to

facts ? Dalton, firm in his conviction that different elements had atoms of different sizes (the very genesis of his theory) could see neither the relevancy of Gay-Lussac's Law of Volumes nor the beauty of Avogadro's explanation. For him the formula of water was always HO. Berthelot, equally firm in his conviction that in chemical reactions we are dealing with equivalents , could see the force of Gay-Lussac's experiments, but not of Avogadro's arguments. For him the formula of water (the molecule occupying two volumes) was H_2O_2." It is obvious that such a conception must have proved a most formidable barrier to progress in the formulation of the structure of organic compounds.

The Constitution of Acenaphthene and of Naphthalic Acid.

With regard to the constitution of acenaphthene Berthelot remarks, "Il joue à l'égard de la naphthalene la même rôle que la styrolene à l'égard de la benzene."

Styrolene (styrene, phenyl ethylene) - $C_4H_2(C_{12}H_6)$ $[C_2H_3.C_6H_5]$

Acenaphthene - $C_4H_2(C_{20}H_8)$ $[C_2H_3.C_{10}H_7]$

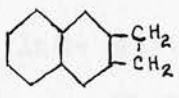
It was not long before the error of this conception was made apparent, though twenty years elapsed between the discovery of acenaphthene and the complete evolution of our present views on its structure.

In 1872 Berthelot and Brady accomplished an interesting synthesis of the hydrocarbon (Compt. rend.,

74, 1463). Ethyl-naphthalene was prepared from bromo-naphthalene, ethyl iodide and sodium. This gave acenaphthene (a) on passing through a porcelain tube heated to bright redness or (b) by heating with bromine at 180°C and treating the product with alcoholic potassium hydroxide.

A further important step was made by Behr and van Dorp (Ann., 1874, 172, 263) when naphthalic acid was obtained by the oxidation of acenaphthene.

The presence of an ethylene bridge was thus clearly shown, but the assumption was made that this occupied the 2:4 positions in the naphthalene nucleus (Formula I)



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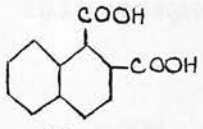

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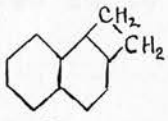
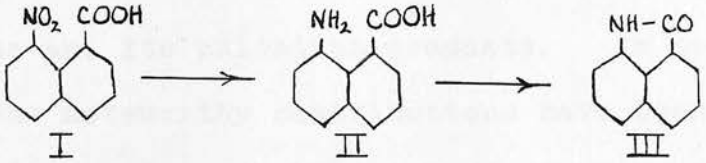


III

Terrisse (Ann., 1885, 227, 133) worked on the naphthalic acid obtained by oxidation of acenaphthene, preparing the compounds analogous to fluorescein and eosin, derived from phthalic anhydride. He opposed the view generally held at that time considering that the ethyl-naphthalene of Berthelot and Brady was the α-compound, and maintaining moreover that the experimental evidence agrees with the formulation of naphthalic acid as an ortho-derivative. He proposed formula II for naphthalic acid and hence III for acenaphthene.

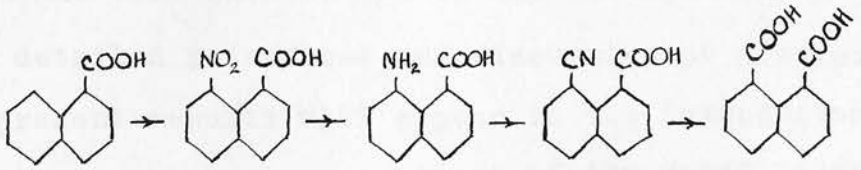
Our present views on the constitution of these compounds were not established till 1887 when

Bamberger and Philip (Ber., 20, 237) synthesised naphthalic acid. The work of Ekstrand (Ber., 1886, 19, 241; J. pr. Chem., [2], 1888, 38, 1131) showed that the 1:8-naphthalene derivatives possess properties resembling those of ortho-derivatives. Bamberger and Philip proposed the term 'peri' for the groups which possess such special characteristics. By the direct nitration of 1-naphthoic acid Ekstrand had obtained two mono-nitro acids which were separated by crystallisation from alcohol. The more soluble isomeride was reduced by alkaline ferrous sulphate to the corresponding amino-acid. The ready formation of naphthostyril (III) from this compound proved it to have the 1:8- structure.



I II III

Bamberger and Philip carried out a Sandmeyer reaction on the 8-amino-1-naphthoic acid, replacing the NH_2 by CN. Hydrolysis of the product led to the formation of naphthalic acid. The complete synthesis is therefore represented as follows:-



The carboxyl groups of naphthalic acid thus occupy the peri-positions and so therefore also does the ethylene bridge of acenaphthene.

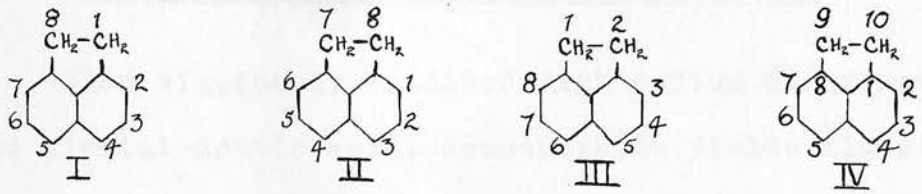
GENERAL SURVEY OF THE ACENAPHTHENE GROUP.

As acenaphthene occurs in coal tar in quantities sufficient to make it of considerable potential value for technical purposes, it has been subjected to quite extensive studies. Its isolation, depending on carefully regulated fractionation and crystallisation of the later portions of the heavy oils or the early runnings of the anthracene oils, is carried out commercially on account of valuable dyes derived from it. The product should be 90-95% pure. The pure hydrocarbon may readily be obtained by recrystallisation from alcohol or benzene.

Most prominent among the early workers in the field is Graebe, who made extensive studies of acenaphthene and its oxidation products. In more recent years some noteworthy contributions have been made to the chemistry of acenaphthene by G. T. Morgan, while Dziewonski at Cracow has published a considerable number of papers on the subject.

It is appropriate at this point to give a brief outline of the more important aspects of the work which has been carried out on the acenaphthene group. More detailed references and discussion of previous and present results will appear in the introductory remarks to the various sections of the experimental work.

Four systems of numbering have been proposed and used from time to time by different workers in the field and in the works of reference.



The system I has been used by Morgan and his co-workers in their extensive contributions to the chemistry of acenaphthene. It possesses the great advantage of obviating the necessity for changing the numbering on passing to compounds of the naphthalene series. This advantage is also possessed by system IV which was proposed by Graebe (Ann., 1903, 327, 77) and used by several later workers (e.g. Zsuffa, Ber., 1910, 43, 2915). Either of these systems is therefore vastly preferable to either II or III. II was used in the 3rd edition of Richter and is adopted by Everest in "The Higher Coal-Tar Hydrocarbons" (Longmans, Green 1927). It is also the official nomenclature of Chemical Abstracts. III is the proposed international numbering and is that used by Beilstein and Chemisches Zentralblatt.

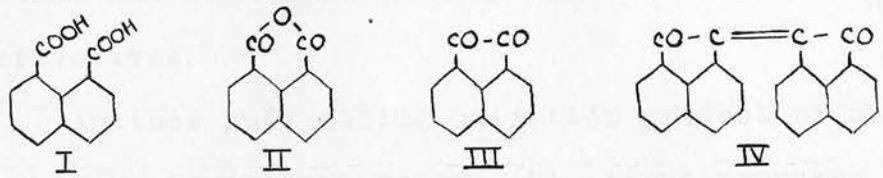
There is little to choose between I and IV. On oxidation of a substituted acenaphthene to a naphthalic acid derivative the specific numberings are no longer required for the carbon atoms of the ethylene bridge

and the advantage in this respect of system IV is only superficial. In the present thesis system I will be adopted to the exclusion of all others.

The Oxidation Products of Acenaphthene.

When vigorously oxidised with sodium dichromate and glacial acetic acid, acenaphthene yields almost quantitatively naphthalic acid (I). Attention has already been drawn to the importance of this reaction in determining the constitution of acenaphthene. Moreover, naphthalic acid is itself a compound of considerable interest for further study. It readily forms the anhydride (II).

Using the same oxidising agent under suitably controlled conditions other products can be obtained. The most important of these is acenaphthenequinone (III).



I II III IV

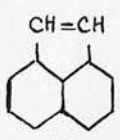
This was first obtained by Graebe and Veillon (Ber., 1887, 20, 659) but not in the pure state. The experimental details were carefully studied by Graebe and Gfeller (Ann., 1893, 276, 1) and though much later work has been done on the subject, the preparative method which they evolved is still the best. As an intermediate in vat-dye manufacture acenaphthenequinone has attained considerable importance. (cf. Colour

Index (edited by Prof. F.M. Rowe), Nos. 1228, 1229, 1230)

Another product of the incomplete oxidation of acenaphthene is biacenaphthylidenedione (IV) which will be discussed at greater length when a new method for its preparation discovered in the course of the present work (p.129), and some further studies on the compound, are described.

Both acenaphthenequinone and biacenaphthylidenedione on stronger oxidation give naphthalic acid. An extremely neat and valuable method for the oxidation of acenaphthenequinone to naphthalic acid is described by Whiston (J. Soc. Chem. Ind., 1924, 43, 370 T). An alkaline suspension of the quinone is treated with hydrogen peroxide, an almost quantitative yield being obtained. In the course of the present work this method has been successfully applied to substituted derivatives.

Another interesting oxidation product of acenaphthene is acenaphthylene (V), first prepared by Behr and van Dorp (Ann., 1874, 172, 263) by passing acenaphthene vapour over red hot lead oxide. The best method now available is stated to be that of Dziewonski and Rapalski (Ber., 1912, 45, 2491) in which acenaphthene vapour in a stream of carbon dioxide is passed through a red-hot silica tube.



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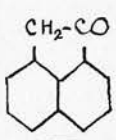

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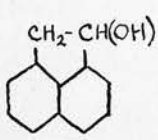


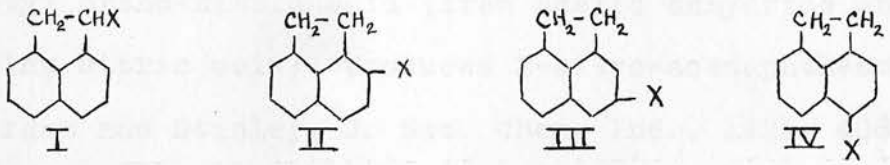
VII

Graebe and Gfeller (loc. cit.) investigated the reduction of acenaphthenequinone. Zinc dust and glacial acetic acid gave a mixture containing acenaphthenone (VI) and acenaphthene, but when the reduction was carried out with hydriodic acid and red phosphorus, biacenaphthylidenedione (IV) was formed. The direct reduction of acenaphthenequinone is not the best method of obtaining acenaphthenone and the problem of the preparation of this compound will be more fully discussed later (p. 96).

An intermediate stage in the reduction between acenaphthenone and acenaphthene was obtained by Braun and Bayer (Ber., 1926, 59, 920). In the catalytic hydrogenation of acenaphthenequinone - using thirty to forty atmospheres of hydrogen at temperatures ranging from 150-250° with nickel as catalyst and tetralin as solvent - acenaphthenol (VII) was obtained. This compound was characterised by its urethane. It has also been obtained by Marquis (Compt. rend., 1926, 182, 1227) from acenaphthene by oxidation with lead peroxide in acetic acid. The yield was less than 30% and no other product was isolated. Marquis further observed that oxidation of acenaphthenol with chromic acid in acetic acid gave acenaphthenone in good yield.

Substituted Derivatives of Acenaphthene.

From the formula of acenaphthene it will be seen that four mono-substituted derivatives are possible



I II III IV

The general tendency is for substitution of one of the peri hydrogen atoms to take place as in IV. Thus 4-chloro-, 4-bromo- and 4-iodo-acenaphthene have been prepared by direct halogenation. Vigorous oxidation of these mono-halogeno-derivatives yields the corresponding naphthalic acids. In the case of the chloro- and bromo-compounds it has been possible to prove the constitution by distillation of the calcium or copper salts of the acids with lime (Graebe and Guinsberg, Ann., 1903, 327, 87; Crompton and Cyriax, Proc. Chem. Soc., 1908, 24, 241). Moreover the three halogenated acenaphthenes have also been obtained by the reduction of 4-nitro-acenaphthene, diazotisation of the resulting amine, and treatment with cuprous chloride, cuprous bromide or potassium iodide respectively (Sachs and Mosebach, Ber., 1910, 43, 2473). The nitration of acenaphthene with concentrated nitric acid in glacial acetic acid yields 4-nitro-acenaphthene. This was proved by oxidation of the product to 4-nitro-naphthalic acid, followed by reduction to 4-amino-naphthalic acid and distillation of the latter with slaked lime to give α-naphthylamine.

(Graebe and Briones, Ann., 1903, 327, 77).

On the other hand it has been observed that anhydrous nitration, using either benzoyl nitrate or acetyl ortho-nitric acid (from acetic anhydride and fuming nitric acid), produces 2-nitro-acenaphthene. (Morgan and Stanley, J. Soc. Chem. Ind., 1925, 408 T; Morgan and Harrison, ibid., 1930, 413 T) A similar effect was previously shown to be present in the case of the sulphonation of acenaphthene. Under anhydrous conditions (chlorosulphonic acid in an inert solvent) acenaphthene 2-sulphonic acid is formed (Dziewonski and Stolywho, Ber., 1924, 57, 1531) With sulphuric acid the 4-isomeride is obtained.

As a final example of the direct introduction of a single substituent into the acenaphthene nucleus some applications of the Friedel-Crafts reaction may be mentioned. Again it is observed that the main tendency is to form peri-substituted derivatives. Graebe and Haas (Ann., 1903, 327, 91) condensed acenaphthene with acetyl chloride and with benzoyl chloride respectively, in presence of aluminium chloride. The product in each case was the 4-compound. Later work has been carried out on these compounds by Dziewonski and his co-workers (Ber., 1925, 58, 2239; Bull. intern. acad. polon, 1932 A, 288; C, 33, I, 2250). Dziewonski has also investigated the condensation of acenaphthene with propionyl chloride, substitution taking the expected course. 4-Chloro-

acetyl acenaphthene has been described by Mayer and Kaufmann (Ber., 1920, 53, 289). The same workers also condensed acenaphthene with ethyl bromide in carbon disulphide solution in the presence of aluminium chloride, thus preparing 4-ethyl-acenaphthene. It is of interest to note, however, that with benzyl chloride Dziewonski and Leonhard (C., 29, I, 1338) did not obtain α-benzyl-acenaphthene exclusively, smaller quantities of the β-compound being also formed.

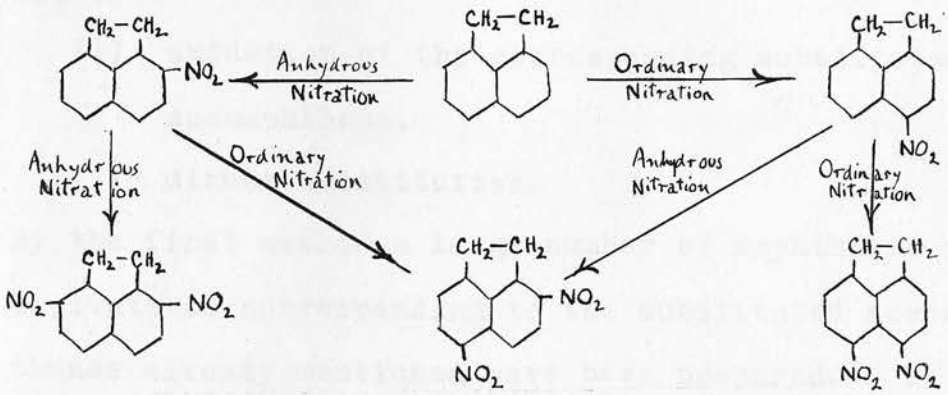
After this somewhat detailed survey of the direct introduction of single substituents into the acenaphthene nucleus, it remains to draw attention to the considerable number of mono-substituted derivatives which have been obtained from these compounds by further changes. Thus as a result of the recent systematic investigations of Morgan and his co-workers (J. Soc. Chem. Ind., 1924, 343 T; 1925, 408 T, 493 T, and 513 T; 1930, 413 T) all the theoretically possible mono-amino-acenaphthenes are known. The same workers, particularly Morgan and Harrison (J. Soc. Chem. Ind., 1930, 413 T), have also been responsible for the preparation of several new halogen and hydroxy derivatives.

An interesting monosubstituted derivative for the preparation of which a variety of methods has been described is acenaphthene-4-carboxylic acid.

Having thus briefly summarised our state of knowledge with regard to the mono-substituted derivatives the introduction of a second substituent may be considered.

Two disulphonic acids have been described by Dziewonski and Stolywho (loc. cit.) but they have not yet been definitely characterised.

On further nitrating 4-nitroacenaphthene a second nitro group enters the other peri-position to give 4:5-dinitro-acenaphthene when ordinary nitration methods are used, but under anhydrous conditions the 2:5-dinitro-compound is formed. In the case of 2-nitro-acenaphthene, 2:7-dinitro-acenaphthene is formed under anhydrous conditions and 2:5-dinitro-acenaphthene by ordinary nitration. It should be noted however that in the anhydrous nitrations, entry of the second nitro-group does not take place exclusively in the ortho-position. These reactions may be summarised thus:- (Morgan and Harrison, J. Soc. Chem. Ind., 1930, 413 T)



Nitration of 4-bromoacenaphthene leads to the production of 4-bromo-5-nitroacenaphthene, as has been shown by Dziewonski, Schoen and Glazner (Bull. intern. acad. polon., 1929 A, 636; C., 30, I, 2559). Similarly the nitration of acenaphthene-4-sulphonic acid yields 5-nitro-acenaphthene-4-sulphonic acid. (Morgan and Yarsley, J. Soc. Chem. Ind., 1925, 513 T)

On the other hand when 4-formylamino- or 4-acetyl-

amino-acenaphthene is nitrated the nitro group enters the 3-position.

It is thus seen that while the second group tends generally to enter a peri-position, this is not invariably the case. Reaction conditions or the nature of the substituent already present may determine the course of the reaction otherwise.

Substituted Derivatives of the Oxidation Products of Acenaphthene.

(i) Naphthalic Anhydride.

In the preparation of substituted derivatives of naphthalic anhydride there are two main lines of approach:

(i) oxidation of the corresponding substituted acenaphthene,

(ii) direct substitution.

By the first method a large number of naphthalic acid derivatives corresponding to the substituted acenaphthenes already mentioned have been prepared. It is obvious that the compounds so obtained will be substituted almost exculsively in one or both of the peri-positions. Some of them have already been mentioned and a fuller account need not be given here. Attention may be drawn to the somewhat surprising fact that 2-nitroacenaphthene could not be oxidised to the corresponding naphthalic acid under conditions applicable to 4-nitroacenaphthene (calcium permanganate in

acetone). The oxidation has however been accomplished using dichromate and acetic acid (Morgan and Harrison, J. Soc. Chem. Ind., 1930, 413 T). Naphthalic acid derivatives substituted in the 2-position have also been obtained by Dziewonski, Kocwa and Geschwindowna (Bull. intern. acad. polon., 1928 A, 405) from acenaphthene-2-sulphonic acid. Oxidation of the latter gave 2-sulpho-naphthalic acid, from which the hydroxy-acid was obtained by alkaline fusion and the chloro-acid by treatment with phosphorus pentachloride.

Direct substitution of naphthalic anhydride leads as a general rule to compounds substituted in the 3-position, the meta-directing influence of the carboxyl group overcoming in this particular case the normal tendency towards peri-substitution in the naphthalene nucleus. Thus sulphonation and nitration lead to 3-sulpho-and 3-nitro-naphthalic acids respectively (Anselm and Zuckmayer, Ber., 1899, 32, 3284; Graebe and Briones, Ann., 1903, 327, 84). Various substituted derivatives are described by Francesconi and Bargellini (Gazz., 1902, 32, 2 , 90). Among these is a mono-bromo-naphthalic anhydride in which it was concluded that substitution had taken place in the 4-position. Part of the present work is concerned with the proof that it is actually 3-bromonaphthalic anhydride which is formed.

With regard to the introduction of a second substituent into a mono-substituted naphthalic acid

the information which we at present possess is somewhat scanty. It has clearly been shown (Rule and Brown, J. Chem. Soc., 1934, 171) that 3-nitro-naphthalic anhydride on further nitration gives 3:6-dinitro-naphthalic anhydride, but beyond that little has been done. An account will be given in the present thesis of some investigations on the further substitution of several mono-substituted naphthalic anhydrides.

(ii) Acenaphthenequinone.

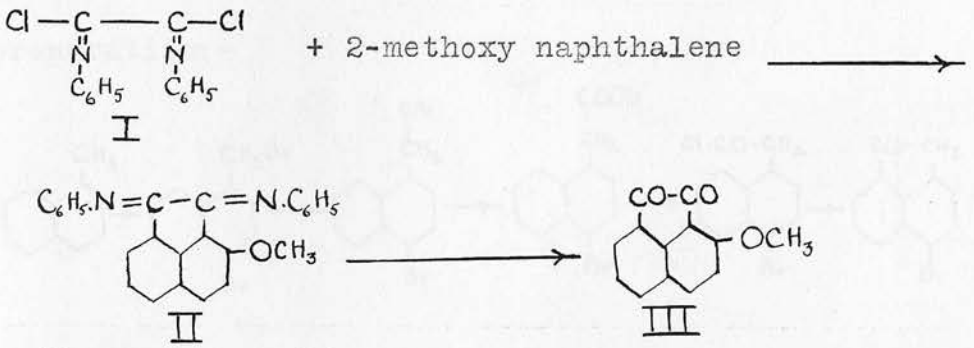
The number of substituted acenaphthenequinones known is comparatively small. Again there are two main lines of approach as in the case of substituted naphthalic acids. Here, however, the oxidation of the substituted acenaphthene must be controlled to give the desired product and this presents a difficult experimental problem. Even under the best conditions the yields are small, although 4-chloro-and 4-bromo-acenaphthenequinone and a few other derivatives have been obtained by this method. It is of interest to note that no nitroquinone has ever been isolated by the oxidation of 4-nitro-acenaphthene.

The literature contains very few references to the direct substitution of acenaphthenequinone. The nitration has been studied by a number of investigators (Mayer and Kaufmann, Ber., 1920, 53, 289; Rowe and Davies, J. Chem. Soc., 1920, 1344). The mono-nitro derivative has not been at all well characterised though

undoubtedly the nitro-group enters the 4-position (Rule and Brown, J. Chem. Soc., 1934, 171). Sircar and Guha (J. Chem Soc., 1924, 335) were unable to repeat the preparation successfully, and invariably found the product to contain dinitro-acenaphthene-quinone. The latter compound can be readily prepared.

With regard to the direct introduction of other substituents the only references found relate to unsuccessful attempts to carry out the bromination. (Mayer and Kaufmann, Ber., 1920, 53, 289; Mayer and Schoenfelder, Ber., 1922, 55, 2972)

An interesting indirect method of obtaining substituted acenaphthenequinones was worked out by Standinger, Goldstein and Schlenker (Helv. Chim. Acta, 1921, 342). While the condensation of oxalyl chloride with naphthalene and its derivatives was not found practicable oxalic acid phenylimidechloride (I) was successfully employed. In this way 2-methoxy acenaphthenequinone III was obtained in good yield.

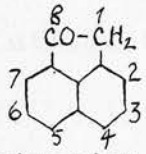


I II III

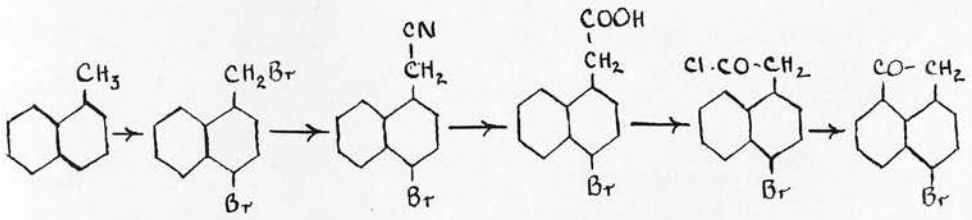
Further work on this last compound has been carried out by Davies, Heilbron and Irving (J. Chem, Soc.,

1932, 2715). On nitration, 6-nitro-2-methoxy-acenaphthenequinone is formed. Oxidation gave 6-nitro-2-methoxy-naphthalic anhydride, which was also obtained by the direct nitration of 2-methoxy-naphthalic anhydride. The entry of the nitro group into the 6-position, while expected in the latter case, is rather surprising in the case of the quinone, for by analogy with the nitration of the unsubstituted compound substitution in the peri- (5-) position appears most probable. Reference is made later in the present thesis (p. 55) to the methods used by these writers in determining the orientation of the disubstituted naphthalic anhydride.

(iii) Acenaphthenone.



Only one acenaphthenone derivative substituted in the nucleus is known namely 4-bromoacenaphthenone. This was obtained indirectly by Mayer and Sieglitz (Ber., 1922, 55, 1835) in a manner which proves its constitution. The following were the steps in its preparation:-



In the present thesis attention has been directed particularly to substituted derivatives of the oxidation products of acenaphthene, while work leading to improved methods for the preparation of acenaphthenone, and incidentally biacenaphthylidenedione, is also described. The method of presentation is such that the experimental work has been divided into sections, each being preceded by a short introduction and discussion of the results.

I THE MONO-BROMINATION OF ACENAPHTHENEQUINONE.

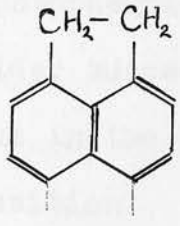
Acenaphthene when brominated in boiling chloroform (Graebe and Guinsberg, Ann., 1903, 327, 87) or in boiling ether (Blumenthal, Ber., 1874, 7, 1092; Crompton and Walker, Chem. Soc. Trans., 1912, 958) gives a mono-bromo-derivative. Oxidation of the latter yields, in proportions varying according to the conditions, 4-bromo-naphthalic anhydride, 4-bromo-acenaphthenequinone and 4:4'-dibromo-biacenaphthylidenedione, recent work on this oxidation being recorded by Dziewonski, Schoen and Glazner (Bull. intern. acad. polon., 1929 A, 636). The proof of the position of the bromine atom in these compounds depends on the fact that α-bromonaphthalene is obtained on distilling the calcium salt of the bromo-naphthalic acid with lime.

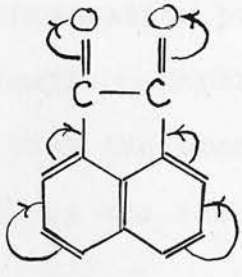
Whilst the bromination of acenaphthene proceeds readily, it is to be expected on theoretical grounds that greater difficulty will be experienced in intro-

ducing bromine directly into the nucleus of acenaphthenequinone, or of naphthalic anhydride. According to present views on the electronic mechanism of organic reactions, the carbon atom in the grouping C=C (as found in the benzene nucleus, etc.) is regarded as anionoid or electron-donating. On the other hand the carbon atom in C=O is kationoid or electron-accepting. The anionoid properties of the C=C group are emphasised in the group N-C=O but diminished in the case of C=C-C=O. This is explained by an electromeric change in the latter system represented by $C\overset{\curvearrowright}{=}O$. This change leaves the carbon atom of the carbonyl group with an electron deficit that can, in part at least, be made up by the anionoid group C=C. We thus have the condition

$$C \overset{\curvearrowright}{=} C - C \overset{\curvearrowright}{=} O$$

In such an effect several C=C groups can be interposed and the kationoid character of the C=O group transmitted from one part of the molecule to another. In the case of acenaphthene the 4- and 5- carbon atoms are strongly anionoid but in acenaphthenequinone the reactivity consequent on this property is reduced by electronic changes, as indicated:-



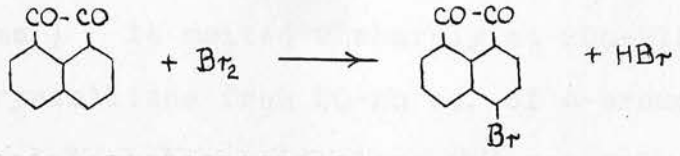


It was thus not surprising to find that attempts to brominate acenaphthenequinone in solution in chloroform or glacial acetic acid, or in chloroform with pyridine present, led invariably to the quantitative recovery of unchanged acenaphthenequinone. Several more vigorous methods, e.g. bromine and acetic acid in a sealed tube at 150°, gave no better results. After these preliminary experiments had been made, records of unsuccessful attempts by other workers were found. Mayer and Kaufmann (Ber., 1920, 53, 289) briefly refer to the introduction of bromine into the acenaphthenequinone nucleus, but state that no uniform product could be isolated. The experimental details are not given. Research on the subject was continued however, and Mayer and Schoenfelder (Ber., 1922, 55, 2972) found that with bromine in nitrobenzene at 200° naphthalic anhydride was formed. Bromine alone or nitrobenzene alone did not effect this oxidation. In chlorobenzene the quinone was recovered unchanged. These workers therefore abandoned attempts to brominate acenaphthenequinone and focussed attention on the determination of the position of the bromine atom in Ciba red R. This dyestuff is obtained by the bromination of Ciba scarlet G - the condensation product of acenaphthenequinone and thioindoxyl. Mayer and Schoenfelder succeeded in showing that the bromine atom is present in the acenaphthene nucleus and occupies a peri-position.

In the course of the present work it has been found that bromination of acenaphthenequinone using bromine in a sealed tube without a solvent gave a product from which a bromoacenaphthenequinone was eventually isolated in the pure state. This however is not a convenient preparative method. An experiment in which acenaphthenequinone was boiled under reflux with excess of bromine led to the formation of the same compound. By varying the conditions in the latter experiment it has now been found possible to obtain the bromoacenaphthenequinone readily in good yield. It has been established that the product is 4-bromoacenaphthenequinone, identical with the compound obtained by the oxidation of 4-bromoacenaphthene. The yield in this oxidation both as recorded in the literature and as at present found is however poor. (Maximum, 10%) The direct bromination now described is therefore the better preparative method since apart from the higher yield it is more rapid and convenient. Moreover 4-bromoacenaphthenequinone has been characterised only with difficulty, widely varying figures having been published for the melting point of the compound, and also for the melting points of its derivatives. The preparations of several of the latter are described below and the physical criteria of the products agree fairly closely with those of the most recent workers.

Experimental.

Bromination of Acenaphthenequinone.



I Bromination in sealed tube.

5 gm. acenaphthenequinone

1.6 cc. bromine.

The bromine (measured by a graduated pipette) was placed in a small test-tube. This was introduced into a clean, dry Carius tube by holding the latter at an angle and allowing the small tube to slide down gently. The mouth of the small test-tube was then covered with a small pad of glass-wool and the quinone introduced. If these precautions are not taken, the quinone in contact with the liquid bromine forms a hard mass which it is difficult subsequently to remove from the tube. In addition a more uniform product is obtained by the above procedure.

The tube was sealed and placed in a bomb-furnace, the temperature being thereafter raised gradually to 120°C and maintained at 120-130°C for 15 hours. (It was found that higher temperatures gave decomposition with charring whilst shorter times led to incomplete bromination.) The tube was opened with the usual precautions, a considerable pressure of hydrogen

bromide having developed. The crude product was removed to a porcelain basin and heated at 140° to drive off hydrogen bromide and traces of bromine. Weight, 6.5 gms. (Theoretical for monobromination, 7 gms.) It melted unsharply at 205-215°C, and was recrystallised from 20-25 cc. of α-bromonaphthalene (glacial acetic acid alone and several other solvents having been found ineffective for purification). Yellow crystals melting at 220-230° were obtained on filtering and washing with a little alcohol and ether. Weight, 2.6 gms. On one further recrystallisation from glacial acetic acid, the product melted sharply at 237°, this figure being raised to 238° by a second recrystallisation. Yield, 2 gms; m.p., 238°C.

The purest sample, obtained by continued recrystallisations from glacial acetic acid until the melting point underwent no further change, melted at 240°. The figures previously recorded in the literature for the melting point of 4-bromoacenaphthenequinone are:- Graebe and Guinsberg (loc. cit.), 194°; Dziewonski et al (loc. cit.), 235-6°; de Fazi (Gazz., 1923, 53, 499), 236.5-7°; Guha, (J. Chem. Soc., 1931, 582), 238°.

To establish with certainty the identity of the product with that obtained by oxidation of 4-bromoacenaphthene, this last reaction was carried out according to Guha (loc. cit.). A mixed melting point showed the identity of the products.

II Bromination with liquid Bromine.

As a result of several experiments the best method of carrying this out was found to be as follows:-

6 gms. acenaphthenequinone

10 cc. bromine.

The quinone was introduced into a 50 cc. flask, fitted with a ground-in reflux condenser, and the bromine added. There is no reaction in the cold, and on gently shaking the quinone goes completely into solution. The mixture was heated on a water bath at 60-70°C for two to three hours. (In comparative experiments it was found that whether two or three hours were given the purity and yield of the product were the same. If however the time was extended to five hours further bromination occurred and the product was purified only with great difficulty.) Copious evolution of hydrobromic acid gas soon took place. At the end of the stated time the reaction mixture was poured into water which had been acidified with sulphuric acid, and boiled to remove excess of bromine. The acidification of the water is an important detail as it greatly facilitates removal of the bromine, and obviates the possibility of oxidation of the quinone. The crude product was filtered off and dried. Weight, 8.5 gm. (Theoretical, 8.3 gm.) After one recrystallisation from glacial acetic acid it melted at 231-233°. Yield, 6.7 gms. (80% of the

theoretical) The pure compound, m.p., 238°, can be obtained by further recrystallisation.

Either nitrobenzene or chlorobenzene, (as an alternative to glacial acetic acid) can be conveniently used for the recrystallisation of 4-bromoacenaphthenequinone. The compound is sparingly soluble in alcohol, benzene and ligroin.

Derivatives of 4-Bromoacenaphthenequinone.

Phenylhydrazone: Bromoacenaphthenequinone (0.25 gm.) was dissolved in about 60 cc. of boiling absolute alcohol, and the calculated molecular quantity of phenylhydrazine (0.1 cc.), dissolved in 15 cc. alcohol, added to the boiling solution. Boiling was continued for about half-an-hour, the solution, at first yellow, having then assumed a red colour. The volume of the alcohol was reduced by evaporation to about 40 cc. when cooling was allowed to take place. The phenylhydrazone forms beautiful red needles, m.p. 179-180°. This was unchanged by recrystallisation and is the figure given by the more recent workers for the melting point of the phenylhydrazone of 4-bromoacenaphthenequinone.

Phenazine: Bromoacenaphthenequinone (0.5 gm.) was dissolved in 15 cc. glacial acetic acid. o-Phenylene diamine (0.2 gm.) dissolved in 10 cc. glacial acetic acid was added and the mixture boiled for a few

minutes. The azine formed cream-coloured silky needles, m.p. 272°C. (Dziewonski, Schoen and Glazner (loc. cit.) record 261-263°C while Guha (loc. cit.) gives 272°C.)

Oxidation to 4-Bromonaphthalic Anhydride.

This reaction proceeds with remarkable ease and efficiency when hydrogen peroxide is used as the oxidising agent. Whiston (J. Soc. Chem. Ind., 1924, 370 T) applied the method to acenaphthenequinone itself, obtaining a 95% yield of naphthalic acid. In the present instance a convenient form of the reagent was used, namely "hyperol", (cf. Booer, J. Soc. Chem. Ind., 1925, 44, 1137) which is a quite stable compound of urea and hydrogen peroxide, containing 35% of the latter.

Pure bromoacenaphthenequinone (0.5 gm.) was mixed with 5 cc. water and 5 cc. 10% NaOH, and heated to 40°C. "Hyperol" (0.7 gm.) was added and the heating continued for a few minutes. The mixture was diluted to 20 cc. and heated to 70-80°C when complete solution took place, thus showing that oxidation occurred quantitatively. The mixture was further diluted and acidified with dilute hydrochloric acid. After standing for some time the white precipitate was filtered off, and dried. Yield almost quantitative, 0.52 gm. M.p. 222°C. It is remarkable that such a sharp melting point should be obtained at this stage. It appears that ring closure of the bromonaphthalic acid to the corresponding anhydride

must take place very readily. Recrystallisation from alcohol gave the same melting point, 222°C. (For 4-bromo-naphthalic anhydride Graebe records m.p. 210°C. Dziewonski and co-workers have obtained the compound both by the oxidation of 4-bromoacenaphthene and by the oxidation of bromo-derivatives of various polycyclic hydrocarbons derived from acenaphthylene by condensation. The melting points found varied from 210 to 212°C. Mayer and Kaufmann record 215°C, while de Fazi gives 220-221°C. A possible reason for the discrepancies is that even when somewhat impure the compound melts quite sharply.)

4-Bromo-naphthalimide:- Bromo-naphthalic anhydride (0.25 gm.) was boiled with concentrated ammonia (10 cc.) under reflux for 1 hour. The product was filtered off, washed and dried. Without further purification it melted at 300°C. This figure was unchanged by recrystallisation from glacial acetic acid. The only figure found in the literature for the melting point of this compound is that of Dziewonski and Kocwa (Bull. inter. acad. polon., 1928 A, 405). These writers quote 286° but the anhydride from which they started melted at 210° and was therefore not pure.

The mixed melting point with an authentic specimen and the above series of derivatives serve conclusively to characterise the compound obtained by direct bromination of acenaphthenequinone as 4-bromo-acenaphthenequinone.

4-Bromoacenaphthenequinone Monoxime

The literature contains no mention of the monoxime of 4-bromoacenaphthenequinone, and the preparation of this compound was therefore investigated. (See also p. 119) If it were a well-characterised compound, obtainable in good yield, its reduction in the light of work to be described later on the reduction of acenaphthenequinone oxime would have proved interesting. It does not however fulfil these conditions.

4-Bromoacenaphthenequinone (2.5 gm.) was dissolved in 96% alcohol (300 cc.) and 0.7 gm. hydroxylamine hydrochloride dissolved in 50 cc. water added. The mixture was boiled for half-an-hour and the major portion of the alcohol then distilled off. On allowing to crystallise a yellow compound separated. This melted at 195-200°C. Recrystallised from benzene it melted with decomposition at 213-214.5°. Yield poor. Analysis by micro-Dumas method. Found: N, 5.03. $C_{12}H_6O_2NBr$ requires N, 5.07%.

II THE BROMINATION OF NAPHTHALIC ANHYDRIDE.

The literature contains only one reference to the direct bromination of naphthalic anhydride. In 1902 Francesconi and Bargellini (Gazz., 32, [2], 90) studied the influence of substituents on the fluorescence which is shown by naphthalic anhydride in concentrated sulphuric acid. In the course of this work they prepared a number of halogenated and nit-

rated derivatives. The halogenations were carried out in all cases in a mixture consisting of equal weights of oleum and commercial concentrated sulphuric acid. Chlorination gave tri- and tetra-chloro-naphthalic anhydrides, whilst with iodine mono- and tri-substituted derivatives were obtained. With bromine however only a mono-bromo-naphthalic anhydride was isolated, and great difficulty was experienced in its purification, as it contained a considerable amount of unchanged naphthalic anhydride. This compound was assumed to be 4-bromonaphthalic anhydride, identical with that obtained by the oxidation of 4-bromo-acenaphthene (Blumenthal, Ber., 1874, 7, 1092). Francesconi and Bargellini remark - "In complessa sembra identica a quella ottenuta da Blumenthal il quale però non accena che al suo punto di fusiona (210°) e alla sua proprietà di sciogliersi nel benzolo." It would appear from this that a mixed melting point was not carried out with an authentic specimen of 4-bromo-naphthalic anhydride.

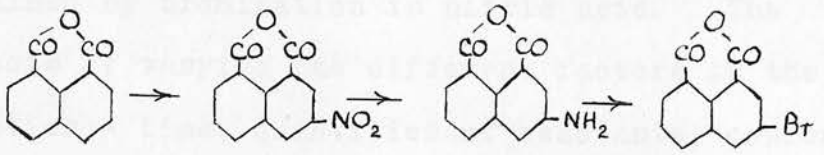
An extensive study of the bromination of naphthalic anhydride has been carried out as part of the present work. In the first experiments performed naphthalic anhydride was heated with one molecule of bromine in a sealed tube. A mono-bromo-naphthalic anhydride was isolated and proved by direct comparison to be different from 4-bromo-naphthalic anhydride. By analogy with the nitration and sulphonation

in which the meta-directing influence of the carboxyl group overcomes the normal tendency to peri-substitution in the naphthalene nucleus, it was suspected that 3-bromo-naphthalic anhydride had been obtained. Moreover there is every reason to expect that the same compound would be formed under the conditions employed by Francesconi and Bargellini. The preparation as described by these authors was therefore repeated. In their original paper they emphasise the difficulty of purification and quote analyses at different degrees of purity. In the present instance however such great difficulties were not experienced and the melting point of the purified product was much higher than that recorded. In fact it coincided with the melting point of the compound obtained by bromination in a sealed tube, and a mixed melting point proved the two compounds to be identical. A few derivatives of the anhydride have been prepared, for comparison with those obtained from 4-bromo-naphthalic anhydride.

To confirm the expectation that the newly-characterised bromo-naphthalic anhydride is the 3-isomeride, a preparation of the latter compound by a method proving its constitution has been carried out.

By the work of Graebe and Briones (Ann., 1903, 327, 77) it has been definitely shown that nitration of naphthalic anhydride gives the 3-nitro derivative. An amino-naphthalic anhydride was obtained by

reduction, and on distillation of this with chalk β-naphthylamine could be isolated. On diazotisation and subsequent treatment with cuprous bromide 3-amino-naphthalic anhydride should give 3-bromo-naphthalic anhydride.



This synthesis has proved successful, and the 3-bromo-naphthalic anhydride obtained by the above scheme of reactions has been shown to be identical with the bromo-naphthalic anhydride obtained directly by the methods already mentioned.

Unfortunately the above synthesis and the sealed tube reactions are of little value as preparative methods. Moreover the method of Francesconi and Bargellini is long and troublesome and the yield is poor. Attention has therefore been directed to methods of preparing 3-bromo-naphthalic anhydride. Various modifications of the last-mentioned method were tried in efforts to improve the yield but without success. As a possible mechanism of the reaction it was thought that sulphonation might precede bromination. This has been definitely proved however not to be the case.

On boiling naphthalic anhydride under reflux with bromine no reaction took place in the absence of a catalyst. On the other hand when iron filings had

been added a tribromo-naphthalic anhydride was formed on prolonged treatment. When attempts were made to stop the reaction before this stage had been reached the product could not be purified.

Interesting and valuable results have been obtained by bromination in nitric acid. The effects of varying the different factors in the reaction - time, quantities of reactants, concentration of acid etc. - have been studied. Though the yield is somewhat low (20%), this constitutes the best preparative method yet available as the time taken is short and under correct conditions the pure product is obtained by direct crystallisation from the reaction mixture.

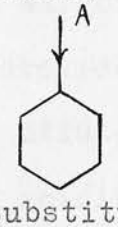
In the course of this study the method used by Waldmann (J. pr. Chem., 1930, 126, 65) for the bromination of phthalic anhydride was applied with slight modifications to naphthalic anhydride. His procedure was to allow bromine (1-1½ mols) to act on sodium phthalate (1 mol) in aqueous solution in presence of sodium hypobromite (1½ mols). In the present instance, 4-bromonaphthalic anhydride was obtained in quite good yield (43%), being characterised by the preparation of its imide, in addition to direct comparison with a specimen of 4-bromonaphthalic anhydride obtained from 4-bromoacenaphthene by oxidation.

In the bromination of naphthalic acid we thus

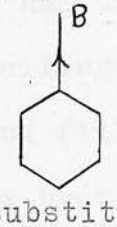
find that the course of the reaction depends on the medium. In an acid medium - concentrated sulphuric or nitric acid - 3-bromo-naphthalic anhydride is formed whereas as just stated bromination in an alkaline medium leads to 4-bromo-naphthalic anhydride. A considerable number of cases in which the normally accepted directive influence of a substituent has been reversed are known in the benzene series. The phenomenon is of considerable interest, both theoretically, and from the more practical aspect as affording methods of preparing otherwise inaccessible compounds. A case in which para-substitution takes place with a typically meta-orienting substituent is reported by Reddelien (Z. ang. Chem., 1922, 35, 580), who obtained an addition compound of benzaldehyde and nitric acid, which gave m-nitrobenzaldehyde on treatment with sulphuric acid, whereas p-nitro-benzaldehyde was formed on treating it with a mixture of acetic anhydride and sulphuric acid. Again meta-substitution may occur with a typically para-orienting group, as was shown by Shoesmith and McGechan (J. Chem. Soc., 1930, 2231), who, in the reaction between toluene and tertiary butyl chloride in presence of $AlCl_3$ or $FeCl_3$, obtained both meta and para compounds, the ratio of the former to the latter being 70 : 30. The case which has however the closest bearing on the results obtained in the course of the present work is the chlorination of benzoic acid. The meta-isomeride is formed in

acid solution (Glund and Kempf, J. Chem. Soc., 1913, 103, 1530), whereas the ortho- and para-compounds are obtained in neutral or alkaline solution. (Hollemann, Die Direkte Einfuhrung von Substituten in den Benzolbern, p. 114) A converse effect has been observed with aromatic amines. (cf. Vorlander and Siebert, Ber., 1919, 52, 283)

Results such as these find a plausible explanation by the recently developed electronic theory of the course of organic reactions, associated with the names of Lapworth, Robinson and Ingold. The orienting influence of a substituent atom is attributed to its electric charge and this conception is readily extended to groups containing polar linkages. Such a substituent has an inductive effect on the nucleus and thereby causes a change in the electron distribution. When the inductive effect is negative an ortho-para-directing effect tends to appear; when it is positive the tendency is to meta-substitution. The two types can be represented as A and B (Robinson)

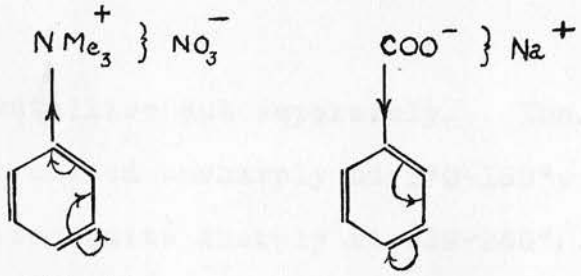


o-p-substituting tendency



m-substituting tendency

A kationic charge will produce a B-type effect, as when meta-substitution takes place with a quaternary ammonium salt. The converse will hold for an aromatic acid in alkaline solution.



m-substitution p-substitution

In the present case of naphthalic acid an extension of the ideas developed for the benzene series can be made to explain the different directing effect in acid or alkaline solution, it being borne in mind that the normal tendency to peri-substitution in the naphthalene nucleus is also a factor in the formation of the 4-bromo compound in alkaline solution.

Experimental

Sealed tube bromination of naphthalic anhydride.

5 gm. naphthalic anhydride

2 cc. bromine.

These were introduced into a Carius tube in the manner already described for the bromination of acenaphthenequinone (p. 25). The tube was then heated to 150 ± 5° for 18 hours. The product was dissolved in slight excess of the calculated quantity of sodium hydroxide solution by boiling for some time, the solution diluted to 500 cc. and filtered. The filtrate was acidified with dilute hydrochloric acid, and after standing for a few hours the product was filtered off, washed free from acid and dried. Weight, 5.5 gm. It was extracted twice with alcohol, 75 cc. being used in each case. The solutions were

allowed to crystallise out separately. The product from the first melted unsharply at 170-180°, that from the second melted quite sharply at 239-240°. The latter product was recrystallised from alcohol, when it melted at 244°. Further recrystallisation did not change this melting point. The compound could be readily sublimed, when it formed beautiful white needles, m.p. 244°. The sublimation was carried out in a crucible 4 cm. high on the sand bath. Particular care was taken in the purification of the above bromo-derivative as it had been observed that this type of compound often melts quite sharply even when impure. A mixed melting point with naphthalic anhydride gave the following result:-

Substance	naphthalic anhydride	naphthalic anhydride + x-bromonaphthalic anhydride	x-bromo-naphthalic anhydride
M.p.	272-3°	215-217°	244°

It is thus apparent that the substance is not impure naphthalic anhydride. A mixed melting point with 4-bromonaphthalic anhydride m.p. 222°, also showed a large depression (mixed m.p. 190-200°).

Preparation of imide.

Bromonaphthalic anhydride (0.1 gm.) was boiled with concentrated ammonia in a beaker for 2 hours, a fresh quantity being added from time to time to make up loss by evaporation. The product was filtered,

washed well and dried. M.p. 316°, unchanged on recrystallisation from glacial acetic acid. (M.p. of 4-bromo-naphthalimide, 300°. Mixed m.p. about 290°.) Analysis by micro-Dumas. Found: N, 4.93. $C_{12}H_6O_2NBr$ requires N, 5.07%.

Bromination of naphthalic anhydride in sulphuric acid.

Ref.- Francesconi and Bargellini, Gazz. 1902, 32, [2], 90.

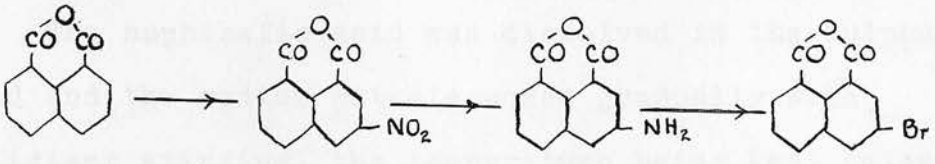
Naphthalic anhydride (20 gm.) was introduced into a mixture of 70 gm. fuming sulphuric acid and 70 gm. commercial concentrated sulphuric acid, in a flask fitted with a ground-in condenser. The mixture was heated for two to three hours at 65-70°, bromine (60 gm.) being added gradually. The temperature was then raised slowly to 200° in the course of seven hours. The mixture was allowed to cool, poured into water, filtered after standing for some time, washed with water till free from acid and dried. Weight, 11 gm. It was recrystallised from 200 cc. acetic anhydride. Yield, 6.3 gm. (25% of theoretical) M.p., 238-241°. (F. and B. record m.p. 211-12° for their purest product, and do not state the yield. For the analysis they give : Found Br, 27.96; C, 49.33; H, 2.61. Calculated Br, 28.75; C, 48.89; H, 2.37.)

The product can be further purified by recrystallisation from acetic anhydride, glacial acetic acid, concentrated nitric acid or alcohol. For

small quantities fractional sublimation under reduced pressure is very suitable.

The pure compound had a melting point of 244°C and was proved by mixed melting point to be identical with the product obtained from the sealed tube bromination which depressed the melting point of 4-bromo-naphthalic anhydride. The compound is therefore not 4-bromo-naphthalic anhydride as was assumed by Francesconi and Bargellini.

Preparation of 3-bromo-naphthalic anhydride.



(a) Preparation of 3-nitro naphthalic anhydride.

Refs.- Graebe and Briones, Ann., 1903, 327, 84.
Leucks, Perkin and Whitmore, J. Amer. Chem. Soc., 1929, 51, 1831.

The nitration described in these papers is essentially the same, though the method of working up the product is different. Graebe and Briones recrystallised from acetic acid. They record m.p. 247°. Leucks, Perkin and Whitmore effected purification by hot toluene (4 cc. per gm. of crude product), and give as the melting-point of the not quite pure product so obtained 247-250°. Further purification from nitrobenzene or glacial acetic acid raised the melting point to 252-3°. In the course of the

present work both methods have been employed, as the following synthesis is not the only one in which the compound has been used. The procedure of the later workers is to be favoured, particularly when large quantities are being prepared. It has been found that the naphthalic acid supplied by B.D.H. consists largely of the anhydride and is suitable for use in this reaction without submitting it to complete dehydration. A typical nitration was as follows:-

50 gm. naphthalic acid .

500 cc. concentrated sulphuric acid.

22 gm. sodium nitrate.

The naphthalic acid was dissolved in the sulphuric acid and the sodium nitrate added gradually with efficient stirring, the temperature being kept below 20°. After the addition was complete, the mixture was heated on the water bath for 15 mins., allowed to cool and poured into ice and water. The crude product was filtered off, washed free from acid and dried. Weight, 62 gm. It was heated to the boiling point with 250 cc. toluene, and the mixture filtered while still hot through a warmed Buchner funnel. The product was washed with a little benzene and dried. Yield, 46 gm. (75% of theoretical) M.p. 248-251°.

(b) Preparation of 3-amino-naphthalic anhydride.

Ref. - Graebe and Briones, Ann., 1903, 327, 77.

10 gm. 3-nitro-naphthalic anhydride

40 gm. stannous chloride

40 gm. concentrated hydrochloric acid.

The 3-nitro-naphthalic anhydride was dissolved in alcohol and added to the stannous chloride dissolved in the concentrated hydrochloric acid. The mixture was heated under reflux till the precipitated nitro-naphthalic acid had gone into solution. The alcohol was then evaporated off, and the residue filtered. The product was heated with sodium carbonate solution till dissolved, the solution filtered and the amino-acid precipitated with acetic acid. Even after standing overnight the compound was still in a finely divided condition and difficult to filter. It was washed well, and dried. Weight, 6 gm. M.p. above 360°.

It is considered that this is probably not the best method of reduction possible for this compound. A more modern reagent such as sodium hydrosulphite or sodium sulphide might be effectively employed. As the compound was only required for the next reaction, however, methods for its preparation were not further studied.

(c) Preparation of 3-bromo-naphthalic anhydride.

A. 5 gm. 3-amino-naphthalic anhydride
2.5 gm. sodium carbonate
1.7 gm. sodium nitrite.

The amino-acid was dissolved in a solution of the carbonate in 75 cc. water, the solution being filtered from a slight residue. To the well-stirred and cooled solution was added 40 cc. of hydrobromic acid solution (39%). The sodium nitrite in 50 cc. water was then added gradually when the diazonium compound formed in brown suspension.

B. 7.2 gm. cuprous bromide
40 cc. hydrobromic acid (39%)
150 cc. water.

These reagents were mixed and heated to boiling point when complete solution of the copper salt took place.

The suspension of the diazonium salt obtained in A was added to the solution B. Vigorous frothing occurred. The mixture was boiled for a few minutes and allowed to stand overnight. On filtering and washing a brown product, weight, 6 gm. which could not be purified by means of solvents, was obtained. Sublimation however gave white needles. The bulk of the product was therefore sublimed under reduced pressure. A small yield of a compound melting at 244° was obtained. A mixed melting point with the compound obtained by the bromination of naphthalic anhydride, a using bromine in a sealed tube and b with bromine in sulphuric acid, proved conclusively

that the latter is 3-bromo-naphthalic anhydride.

Further Experiments on the Preparation of 3-Bromo-naphthalic anhydride.

Bromination by the method of Francesconi and Bargellini described above, but using only concentrated sulphuric acid instead of a mixture of oleum and concentrated sulphuric acid was unsuccessful. Unchanged naphthalic anhydride was recovered. It was therefore thought possible that sulphonation precedes bromination in the stronger acid mixture, and an experiment was carried out to test this.

According to Anselm and Zuckmayer (Ber., 1899, 32, 3283) sulphonation occurs on heating at 90-95° for thirty minutes with fuming sulphuric acid (25% oleum). In the present case naphthalic anhydride was subjected to this treatment, and to the reaction mixture was added, after cooling, a weight of concentrated sulphuric acid equal to the weight of fuming sulphuric acid used. Bromine was then added and the temperature raised as in the previous bromination. When the product was poured into water it was found to be practically completely soluble, proving that under these conditions the sulphonic group is not replaced by a bromine atom.

In another unsuccessful experiment the 3-sulpho-naphthalic acid was isolated (Anselm and Zuckmayer, loc. cit.) and then heated in aqueous solution with

bromine in a sealed tube at 240° - under which conditions the sulphonic groups of anthraquinone sulphonic acids are replaced by bromine atoms (Fierz-David, Helv. Chim. Acta, 1927, 10, 209). In the present case the product was almost completely soluble in water and proved to be unchanged 3-sulpho-naphthalic acid.

Preparation of 3-bromonaphthalic anhydride by bromination of naphthalic anhydride in nitric acid solution.

A number of comparative experiments were carried out using in all cases 5 gm. naphthalic anhydride in 100 cc. of nitric acid at 60-70°. The conditions which remain to be varied are (i) the amount of bromine used, (ii) the concentration of the nitric acid, (iii) the time of heating and (iv) the method of isolating the pure product. By altering one of these variable factors while the others were kept constant, the following conclusions were reached:-

(i) The yield is unchanged whether an atomic proportion or slight excess of a molecular proportion of bromine is used, the probable explanation being that the hydrogen bromide formed in the bromination is at once reoxidised to bromine which is then available to brominate a further quantity of naphthalic anhydride.

(ii) The yield was the same with nitric acid of

d, 1.41 as with d, 1.3. Fuming nitric acid (d, 1.51) gave however an unfavourable result.

(iii) If the time allowed for the interaction is too great (e.g. two hours) the yield is adversely affected. From thirty minutes to one hour was found to be convenient.

(iv) The product could be isolated by pouring into water, and recrystallising from glacial acetic acid. Two recrystallisations were required to obtain the compound perfectly pure. It is better however to cool the reaction mixture, and allow crystallisation to take place from the nitric acid used. In this way, under correct conditions, the pure compound is immediately obtained. Either method gives practically the same yield.

A typical bromination was carried out as follows:-

5 gm. naphthalic anhydride

100 cc. concentrated nitric acid

3 gm. bromine ($1\frac{1}{2}$ atoms)

The anhydride was placed in a 250 cc. flask with ground-in condenser and dissolved in the nitric acid by rapid heating to 70°, solution being assisted by shaking. After slight cooling had been allowed to take place the bromine was added and the mixture maintained at 60-70° on a water-bath, with shaking at first to dissolve the bromine. At the end of half-an-hour the flask was cooled in water, and left over-

night to allow complete crystallisation to take place. The 3-bromo-naphthalic anhydride formed fine white needles which were filtered off and washed well in a sintered glass crucible. M.p. 242-3°. Yield, 1.4 gm. (20% of theoretical). The melting-point was not depressed by an authentic specimen of 3-bromo-naphthalic anhydride.

When the nitric acid filtrate was poured into a large volume of water less than 1 gm. of solid separated and from this by recrystallisation from acetic acid a further small quantity of the bromo-compound could be obtained. No nitro-derivatives of naphthalic acid were detected as by-products of the reaction. It is thus difficult to account for the somewhat poor yield.

Preparation of 4-bromo-naphthalic anhydride by the bromination of naphthalic acid (as potassium salt) in an alkaline medium.

19.8 gm. naphthalic anhydride (0.1 mol.)
28 gm. potassium hydroxide (0.5 mol.)
48 gm. (16 cc.) bromine (0.3 mol.)

A bolt head flask (1 litre) was fitted with a reflux condenser and mercury-sealed stirrer. The naphthalic anhydride was dissolved in a solution of the potassium hydroxide in 250 cc. water by heating and stirring. The solution was cooled in ice and water, and the bromine added gradually in the course of two and a half hours with cooling and stirring.

The temperature of the bath was then raised to 60°C, and the reaction mixture maintained at that temperature for twenty-four hours. An excess of sulphuric acid (500 cc. of 2N acid) was added and after boiling for a short time, the crude 4-bromo-naphthalic acid was filtered off, washed well and dried. Yield, 23.5 gm. It was recrystallised once from nitrobenzene (40 cc.). Yield, 12 gm. (43% of theoretical) M.p., 214-216°.

A mixed melting-point was carried out with an authentic sample of 4-bromo-naphthalic anhydride (m.p. 220°). The figure for the mixed melting-point was 216-218°.

4-Bromonaphthalimide:- This compound is most conveniently prepared by boiling under reflux with concentrated aqueous ammonia. (p. 30) Its preparation was also carried out using urea in a modification of the method given by Waldmann (J. pr. Chem., 1930, 126, 65) for 4-bromophthalimide. In the present case higher temperatures were necessary and the product was slightly more difficult to purify than when obtained by the action of ammonia. The pure 4-bromonaphthalimide obtained by both methods melted at 300-301°.

In addition to the imides, the dimethyl esters and phenylhydrazides of 3-bromo and 4-bromo-naphthalic

anhydrides have been prepared for purposes of comparison. In the case of the 4-isomeride these have already been prepared by Dziewonski and his co-workers. During the present work slight modifications of the procedure have been made and the same conditions have been used in preparing the 3-derivatives.

Preparation of methyl esters.

(Cf. Dziewonski, Geschwindowna and Schimmer, Bull. intern. acad. polon., 1928, A, 507)

5 gm. bromo-naphthalic anhydride

120 cc. 10% sodium carbonate solution

8 cc. dimethyl sulphate.

The bromo-naphthalic anhydride was dissolved in the sodium carbonate solution and the dimethyl sulphate added with shaking. The mixture was heated with occasional shaking for three hours under reflux on a water-bath. To decompose excess dimethyl sulphate and remove unchanged bromo-acid the product was warmed for a short time with 2% sodium hydroxide solution. It was filtered off and washed with hot water. In each case the dimethyl ester could be recrystallised from alcohol.

M.p. of dimethyl-4-bromo-naphthalate, 103° (Dziewonski et al. record 103°)

M.p. of dimethyl-3-bromo-naphthalate, 105°.

The melting point of a mixture of the esters was greatly depressed.

Analysis of dimethyl-3-bromonaphthalate.

Found: Br, 25.1.

Calculated for $C_{14}H_{11}O_4Br$: Br, 24.8%.

Preparation of phenylhydrazides (or phenylhydrazones)

(Cf.- Dziewonski and Kocwa, Bull. intern. acad. polon., 1928, A, 405)

0.25 gm. bromo-naphthalic anhydride

0.12 cc. phenylhydrazine.

The bromo-naphthalic anhydride was dissolved in glacial acetic acid (10 cc.) and the phenylhydrazine added to the warm solution, the mixture being then boiled for half-an-hour. Boiling water was added till a faint cloudiness appeared in the solution. On cooling, the phenylhydrazine derivative crystallised in each case. Purification was effected by recrystallisation from acetic acid.

Francesconi and Bargellini (Gazz., 1902, 32, 90) record 223-4° as the melting point of the derivative from the compound which they believed to be 4-bromo-naphthalic anhydride but which has now been proved to be the 3-isomeride. Dziewonski and Kocwa (loc. cit.) record the same melting point for the derivative from authentic 4-bromo-naphthalic anhydride. The results now obtained were as follows:-

M.p. of compound from 4-bromo-naphthalic anhydride, 231°.

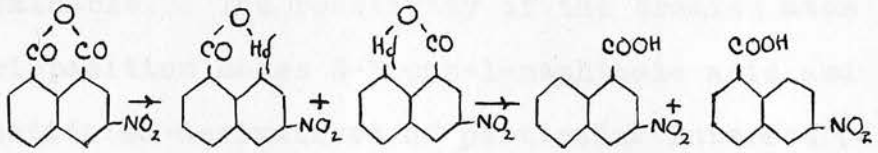
M.p. of compound from 3-bromo-naphthalic anhydride, 223-4°.

Table of Melting-points of 3- and 4-Bromo-naphthalic anhydrides and their Derivatives.

Compound	Melting-point	
	3-bromo	4-bromo
Anhydride	244°	221°
Imide	316-317°	300-301°
Dimethyl ester	105°	103°
Phenylhydrazine compound	223-4°	231°

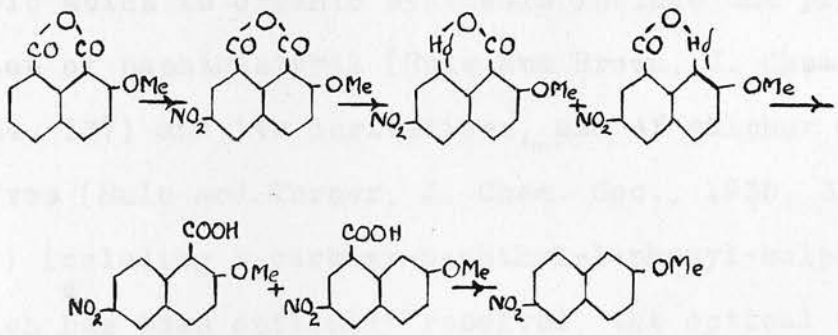
III THE MERCURATION OF SUBSTITUTED DERIVATIVES OF NAPHTHALIC ANHYDRIDE, 3-BROMO-NAPHTHALIC ANHYDRIDE AND 4-BROMO-NAPHTHALIC ANHYDRIDE.

The mercuration of phthalic anhydride was studied by Pesci (Atti. real. acad. Lincei, 1901, [5], 10 I, 362) and the same reaction was applied by Leuck, Perkins and Whitmore (J. Amer. Chem. Soc., 1929, 51, 1831) to naphthalic anhydride and its 3- and 4-mono-nitro derivatives. The nature of the product in each case could be elucidated by boiling with concentrated hydrochloric acid when the mercury was removed with formation of naphthoic acid or its derivatives. With naphthalic anhydride only one product (1-naphthoic acid) is possible, but with a mono-substituted derivative two possibilities arise. For example the mercuration of 3-nitro-naphthalic anhydride gives a mixture of products, from which on hydrolysis both 3-nitro- and 6-nitro-1-naphthoic acid can be isolated.



In the case of 4-nitro-naphthalic anhydride only 4-nitro-1-naphthoic acid can be isolated from the hydrolysis of the mercuration product.

Davies, Heilbron, and Irving (J. Chem. Soc., 1932, 2715) have applied these processes to the elucidation of the constitution of the nitration product of 2-methoxy-naphthalic anhydride. The substituted 1-naphthoic acid obtained was decarboxylated to give an already-known naphthalene derivative - 2-methoxy-6-nitro naphthalene, proving that the nitration had taken place in the 6-position.



The chlorination and bromination of the mercuration product of naphthalic anhydride was investigated by Whitmore and Fox (J. Amer. Chem. Soc., 1929, 51, 3363) and in the hands of later workers this has led to the best method of preparing 8-bromo-1-naphthoic acid, an almost quantitative yield of this compound being now

obtainable. The reactivity of the bromine atom in the peri-position makes 8-bromo-1-naphthoic acid and its substituted derivatives of particular interest (cf. Rule and Barnett, J. Chem. Soc., 1932, 175, 2728). On account of this property these compounds - a number of which have been described by Rule, Pursell and Brown (J. Chem. Soc., 1934, 168) and by Rule and Brown (ibid., 171) - can be used in the preparation of benzanthrones or anthanthrones. By an Ullmann reaction one molecule of the ester of the substituted naphthoic acid can be coupled either with itself or with a molecule of an ortho-halogenated benzoic ester. Hydrolysis and ring-closure results in the respective formation of an anthanthrone or a benzanthrone.

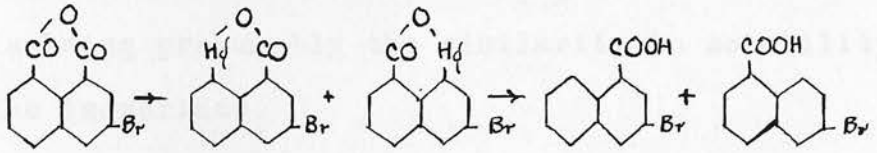
Further applications of the 8-halogenated naphthoic acids in organic synthesis include the preparation of naphthastyril (Rule and Brown, J. Chem. Soc., 1934, 137) and its derivatives, and of sulphur derivatives (Rule and Turner, J. Chem. Soc., 1935, 317, 319) including 8-carboxy-naphthyl-1-phenyl-sulphoxide which has been optically resolved, the optical activity depending on the asymmetry of the sulphoxy group.

An account is given below of the mercuration and further treatment of some substituted naphthalic acids prepared in the course of the present work.

When 4-bromo-naphthalic acid was mercurated, and the product boiled with hydrochloric acid 5-bromo-

naphthoic acid could be isolated from the resulting mixture, the compound being characterised by comparison with an authentic specimen of 5-bromo-naphthoic acid obtained by the bromination of naphthoic acid. No 4-bromo-naphthoic acid was obtained. It thus appears probable that bromine in the 4-position exerts an opposite effect to the nitro- group on the position taken up by the mercury atom, Leuck, Perkins and Whitmore having found as above stated that 4-nitro-naphthoic acid is the chief product from 4-nitro-naphthalic acid. On the other hand, the yield of 5-bromo-naphthoic acid being only 35%, marked differences in the solubilities of the isomeric bromo-naphthoic acid may control the eventual isolation of this compound.

When the same reactions were applied to 3-bromo-naphthalic acid it was again found that only one product could be isolated in the pure state, though a mixture of 3- and 6-bromo-naphthoic acids is obtained.



Since neither of these substituted naphthoic acids is known it was necessary in order to identify the product to synthesise at least one of them by a method leaving no doubt as to the constitution.

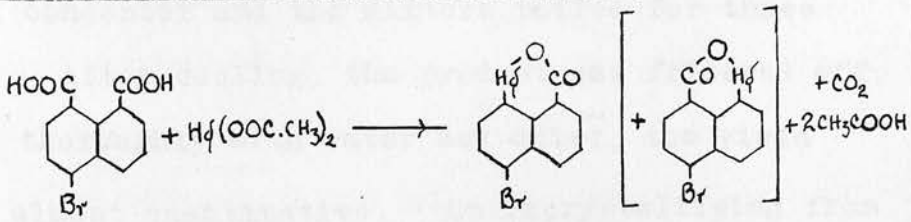
As 3-nitro-naphthoic acid has been made available

by the work of Perkin, Leucks and Whitmore, its reduction with subsequent replacement of the amino-group by bromine gives a method of preparing 3-bromo-naphthoic acid. This has been found practicable and the product identified with that obtained by the hydrolysis of the mercuration compound of 3-bromo-naphthalic acid. It is probable therefore that in this case, as in that of 3-nitro-naphthalic acid the mercury atom predominantly enters the ring which does not contain the substituent.

From the yields of pure 5- and 3-bromo-naphthoic acids (35% and 25% respectively) obtained in the above hydrolyses of the mercuration products, the conclusion may be reached that more nearly equal amounts of the isomeric forms are produced than is the case when the substituent is a nitro- group. When bromination of the mercuration compounds was carried out, in neither case could a pure compound be obtained. This lends support to the conclusion just made, a contributary effect to the difficulty of separation of the dibromo-acids being presumably the similarity in solubility of the isomerides.

Experimental

Mercuration of 4-Bromo-naphthalic acid.



18.5 gm. 4-bromo-naphthalic anhydride

5.5 gm. sodium hydroxide

14.5 gm. mercuric oxide.

The 4-bromo-naphthalic anhydride was dissolved in a solution of the sodium hydroxide in 500 cc. water in a 1-litre Pyrex flask fitted with a reflux condenser. The mercuric oxide was dissolved in 15 cc. glacial acetic acid and 40 cc. water, the solution being added to the contents of the flask. A white suspension of 4-bromo-naphthalic acid formed, and the mixture was then made distinctly acid with acetic acid.

After boiling for 100 hours, the product was filtered off, washed with water, alcohol and ether, and dried in a hot-air oven. Yield, 28 gm. (93% of the theoretical.)

In an experiment, in which mechanical stirring was employed and the time of boiling reduced to 20 hours, it was found that mercuration had not been effected.

Hydrolysis of mercuration-product.

10 gm. mercuration product

200 cc. concentrated hydrochloric acid

200 cc. water.

The above were mixed in a flask fitted with a reflux condenser and the mixture boiled for three hours. After cooling, the product was filtered off, washed thoroughly with water and dried, the yield being almost quantitative. On recrystallising from

50 cc. glacial acetic acid, the product melted unsharply at 220-230°. A second recrystallisation raised the melting point to 248-257°. On a third recrystallisation quite a sharp melting point, 256-258°, was obtained, the yield being 2 gm. (35% of the theoretical).

Since 4-bromo-naphthoic acid melts at 212° (Mayer and Sieglitz, Ber., 1922, 55, 1835) or 217-220° (Gomberg and Blicke, J. Amer. Chem. Soc., 1923, 45, 1765), whilst 5-bromo-naphthoic acid prepared by the bromination of naphthoic acid melts at a much higher temperature, Eckstrand (J. pr. Chem., 1888, 38, 155) reporting 248°, it appears probable that the bromo-naphthoic acid above obtained is identical with the latter. Confirmation of this has been obtained by comparison with the product of direct bromination of naphthoic acid. This was prepared according to Eckstrand (loc. cit.) and found to have a much higher melting point (260°) than that reported. The mixed melting point with the compound, m.p. 256-8°. was 257-9°.

Mercuration of 3-bromo-naphthalic acid.

8.3 gm. 3-bromo-naphthalic anhydride

2.5 gm. sodium hydroxide in 250 cc. water

6.5 gm. mercuric oxide in 10 cc. glacial acetic acid and 20 cc. water.

Since the procedure followed was the same as in

the case of 4-bromo-naphthalic acid the details need not be repeated. The yield of mercuration product obtained was 12.5 gm. (95% of the theoretical).

Hydrolysis of mercuration product.

8 gm. mercuration product

100 cc. concentrated hydrochloric acid

100 cc. water.

The above were mixed and the mixture boiled under reflux for two hours. After cooling the product was filtered off, washed and dried. Yield 4.3 gm., almost quantitative.

After four recrystallisations from glacial acetic acid the product melted sharply at 231-2° and this melting point was not changed by a further recrystallisation from benzene. From the glacial acetic acid filtrates, which were combined and poured into water, a further quantity of the same compound could be obtained by recrystallisation from benzene. Total yield, about 1 gm. (23% of the theoretical) M.p. 231-2°.

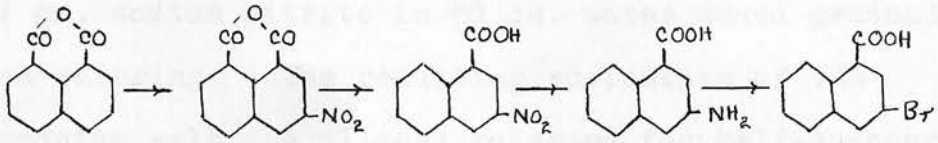
It was found that the acid could be conveniently titrated in 95% alcoholic solution with standard sodium hydroxide using phenolphthalein as indicator. 0.2028 gm. acid required 8.28 mls. of 0.0957 N. NaOH.

$$\text{Molecular weight of acid} = \frac{.2028 \times 1000}{8.28 \times .0957} = \underline{256}.$$

Calculated for $C_{11}H_7O_2Br$ = 251.

Preparation of 3-bromo-naphthoic acid.

The stages in the preparation are as follows:-



The nitration of naphthalic anhydride has already been described (p. 42). The 3-nitro-naphthalic anhydride obtained was mercurated, and 3-nitro-naphthoic acid isolated from the mixture of 3- and 6-nitro-naphthoic acids obtained on hydrolysis. The reactions were carried out as described by Leuck, Perkins and Whitmore (J. Amer. Chem. Soc., 1929, 51, 1831) and, as their results with respect to yields, properties etc., were confirmed, an account of these stages of the preparation need not be given here. Though these authors also carried out the reduction of 3-nitro-naphthoic acid, they do not give experimental details. It is stated however that the isolation of the free amine was difficult. For the present purpose this was however considered unnecessary and the preparation of 3-bromo-naphthoic acid from the 3-nitro-acid was finally carried out as follows:-

The 3-nitro-naphthoic acid (2 gm.) was dissolved in sodium hydroxide solution (4 gm. in 80 cc. water) and the solution heated to the boiling point. Sodium hydrosulphite (5.5 gm.) was added and the mixture boiled for five minutes. Reduction being then considered complete, hydrobromic acid (50 cc. of 39%

solution) was added and the mixture boiled. After a few minutes it was cooled to 0° and a solution of 0.7 gm. sodium nitrite in 50 cc. water added gradually with stirring. The resulting suspension of the diazonium salt was allowed to stand for half-an-hour.

Meanwhile cuprous bromide (3 gm.) was dissolved in 150 cc. water containing 50 cc. hydrobromic acid (39% solution). This solution was heated almost to the boiling point and the diazo solution added. Vigorous frothing took place, and when this had subsided somewhat the mixture was boiled for a few minutes and left to stand overnight. The crude 3-bromo-naphthoic acid was filtered off. Yield, 1.5 gm., pale brown in colour. It was found that purification by means of solvents was unsatisfactory. The pure 3-bromo-naphthoic acid could however be conveniently isolated by sublimation either at ordinary or reduced pressure. It was found to be advantageous in this sublimation to mix the crude product with about four times its weight of graphite, the latter serving to distribute the heat evenly, and to prevent local melting. The purified 3-bromo-naphthoic acid melted at 237-8°. Yield, 0.3 gm.

Other means of reduction such as ferrous sulphate and ammonia were tried before the above method was evolved, but were found to be unsatisfactory.

Though the melting point of the bromo-naphthoic

acid obtained by hydrolysis of the mercuration product of 3-bromo-naphthalic anhydride was not raised above 231-2° even by sublimation, a mixed melting point with the authentic 3-bromo-naphthoic acid prepared above (m.p. 237-8°) gave an intermediate value (234-6°). Absolutely to confirm the identity the methyl ester was prepared from samples of the acid from both sources, the procedure in each case being the same.

Preparation of Methyl 3-bromo-1-naphthoate.

0.25 gm. bromo-naphthoic acid
5 cc. thionyl chloride
10 cc. methyl alcohol.

The acid chloride was prepared by boiling the acid with the thionyl chloride under reflux in a small flask with a ground-in condenser. After evolution of hydrochloric acid had ceased the thionyl chloride was boiled off, first under ordinary pressure, and then in vacuo to remove the last traces. The acid chloride thus obtained was a brownish oil.

The methyl alcohol was added cautiously to the acid chloride when effervescence, with evolution of hydrogen chloride, took place. The contents of the flask were then boiled under reflux for one hour and the alcohol finally removed by evaporation. The ester obtained was recrystallised from aqueous ethyl alcohol.

Both in the case of the authentic 3-bromo-naphthoic acid and that of the bromo-naphthoic acid obtained from the hydrolysis of the mercuration product of 3-bromo-naphthalic anhydride a yield of 0.15 gm., and a melting point of 59° was obtained. The melting point of a mixture of the two was not depressed.

Analysis.

Found: Br, 30.6.

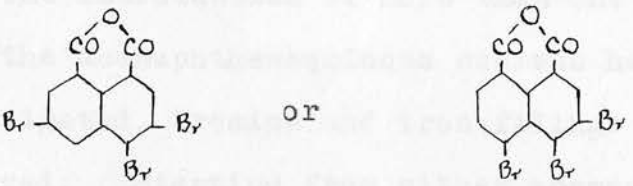
Calculated for $C_{12}H_8O_2Br$: 30.3%.

IV DERIVATIVES OF ACENAPHTHENEQUINONE AND OF NAPHTHALIC ANHYDRIDE CONTAINING MORE THAN ONE SUBSTITUENT IN THE NUCLEUS.

(A) Tribromo-Derivatives of Naphthalic Anhydride and Acenaphthenequinone

In the course of the investigations on the bromination of naphthalic anhydride already described, it was observed that this compound was unaffected when treated under reflux with excess of boiling bromine alone, but that if iron filings were present bromination took place readily. Following up this observation it has been found that on prolonged treatment a tribromo-naphthalic anhydride can be obtained in good yield. Attempts to stop the reaction before this stage was reached however, led to the formation of mixtures from which no intermediate product could be isolated. Work has been carried out in the hope

of obtaining derivatives from the tribromo-naphthalic anhydride, which would assist in the elucidation of its structure but success has not been attained in this respect. At present it may reasonably be formulated as either



the former being considered more probable.

The compound was found to be very stable to heat, prolonged heating above the melting point causing neither decarboxylation nor other extensive decomposition.

Oxidation by means of potassium permanganate, substantially according to the method applied by Graebe and Leonhardt (Ann., 1896, 290, 218) to naphthalic anhydride itself, did not lead to the isolation of any degradation products. It is probable that the substituents so increase the ease of oxidation of the rings that extensive disruption of the molecule occurs.

Though mercuration was successfully carried out as already described for the monobromo-naphthalic anhydrides, hydrolysis of the mercuration product gave a mixture of tribromo-naphthoic acids which could not be separated, presumably because nearly equal amounts of the two possible isomerides were formed. Attempts to decarboxylate the mixture of bromo-naphthoic acids

using copper bronze and boiling quinoline also met with no success.

It has been considered unnecessary to give any more detailed account below of these unsuccessful experiments.

The introduction of more than one atom of bromine into the acenaphthenequinone nucleus has also been investigated, bromine and iron filings being again employed. Starting from either acenaphthenequinone or the 4-bromo-derivative, a tribromo-compound which could be purified only with difficulty was obtained. Modification of the treatment with a view to isolating a dibromo-acenaphthenequinone led to a mixture of products which could not be separated. On the other hand, on prolonged treatment a substance which analysis proved to be a tetrabromo-acenaphthenequinone was formed in small amount, the main product appearing however to be the tribromo-compound.

When the tribromo-acenaphthenequinone was oxidised with hydrogen peroxide in an alkaline medium, a tribromo-naphthalic anhydride, identical with that obtained by the direct bromination of naphthalic anhydride, was isolated.

Experimental

Preparation of tribromo-naphthalic anhydride.

10 gm. naphthalic anhydride

20 cc. bromine

2 gm. iron filings.

The naphthalic anhydride was placed in a 50 cc. flask fitted with a ground-in condenser, and the bromine added. To the solution which formed, the iron filings were added carefully, with cooling in water as required. When the addition was complete the flask was placed in a water bath and the temperature raised to 70°. Heating was continued for 15 hours, the contents of the flask being then poured into 1-1½ litres of water acidified with sulphuric acid. The excess of bromine was removed by boiling and the crude product filtered off and washed well with water. The solid was extracted for about half-an-hour with boiling sodium carbonate solution (6 gm. in 1½ litres of water), the solution of the sodium salt being filtered hot from a small amount of brownish residue. On cooling the filtrate, the sodium salt crystallised out, but only partially and sodium chloride was added to complete the separation. The sodium salt was filtered off, and the filtrate then gave no further precipitate with sodium chloride, though subsequent acidification precipitated a small amount of a white solid, probably the mono- or dibromo-compound or a mixture of these. Purification of the tribromo-compound was effected by recrystallisation of the sodium salt from the minimum quantity of boiling water, when it was obtained as white, lustrous plates. Yield, 18 gm. The purified sodium salt was dissolved in hot water and slight excess of dilute hydrochloric acid added.

The tribromo-naphthalic acid obtained was filtered off, washed and dried. On recrystallisation from acetic anhydride the anhydride obtained melted at 232°, no change taking place on further recrystallisation. Yield, 13 gm. (nearly 60% of theoretical)

Analysis:

Found: Br, 54.94%

Calculated for $C_{12}H_3O_3Br_3$: Br, 55.14%.

Preparation of tribromo-naphthalimide.

Tribromo-naphthalic anhydride (1 gm.) was boiled under reflux for one hour with 100 cc. of concentrated ammonia (d, 0.88). The product was filtered off, washed well with water and dried. Yield, quantitative. M.p. 340°. On recrystallisation from glacial acetic acid in which the substance is somewhat sparingly soluble, 400 cc. being required, long white needles, possessing the same melting point, were obtained.

Analysis by micro-Dumas method.

Found: N, 3.4.

Calculated for $C_{12}H_4O_2NBr_3$: N, 3.23%.

Preparation of tribromo-acenaphthenequinone.

4-Bromo-acenaphthenequinone (2 gm.) and bromine (5 cc.) were placed in a 50 cc. flask fitted with a ground-in condenser, and iron filings (1 gm.) added carefully. The mixture was heated for two hours on a water bath at 60-70°, and then poured into a litre of water acidified with sulphuric acid, the flask

being washed out with further small quantities of water. After boiling to expel the excess bromine, the solid product was filtered off, washed and dried. On recrystallisation from 150 cc. glacial acetic acid, fine yellow needles of a product melting about 240° were obtained (Weight, 2.4 gm.). In addition to glacial acetic acid, nitrobenzene and monochlorobenzene were also found to be suitable solvents for recrystallisation. After several recrystallisations involving considerable loss, the melting point, though not quite sharp, was unaffected by further treatment, a probable explanation being that a small proportion of a more sparingly soluble tetrabromo-derivative is present. Yield, 1.2 gm. M.p., 253-6°.

Analysis:

Found: Br, 57.7.

Calculated for $C_{12}H_3O_2Br_3$: Br, 57.3%.

In the above preparation, instead of starting from 4-bromo-acenaphthenequinone, acenaphthenequinone itself may be used, the first stage of the bromination being carried out over a period of two hours without the presence of iron filings. After allowing the mixture to cool the procedure was then as above.

Tetrabromo-acenaphthenequinone: When the above bromination was prolonged until hydrogen bromide was evolved only in very small amount (about twenty hours), the product after a large number of recrystallisations was

a small quantity of a compound melting at 300-305° and crystallising in fine yellow needles from glacial acetic acid. It was much less soluble in the latter solvent that the tribromo-compound above described. On account of the small yield resultant on the difficulty of purification, the compound has not been further investigated.

Analysis:

Found: Br, 64.7.

Calculated for $C_{12}H_2O_2Br_4$: 64.25%.

Phenazine of tribromo-acenaphthenequinone:- The tribromo-quinone (0.5 gm.) was dissolved in 50 cc. of boiling glacial acetic acid and a solution of o-phenylenediamine (0.15 gm.) in 10 cc. glacial acetic acid added. The compound immediately separated as an almost white curdy precipitate. After boiling for a few minutes, the mixture was allowed to cool. The phenazine was pale cream in colour and melted at 303°.

Analysis by micro-Dumas method.

Found: N, 6.0.

Calculated for $C_{18}H_7N_2Br_3$: N, 5.7%.

Oxidation of tribromo-acenaphthenequinone.

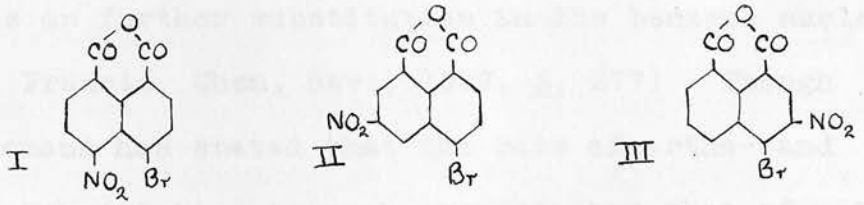
The tribromo-quinone (1 gm.) was suspended in 10 cc. water and 10 cc. of 10% sodium hydroxide solution added. The suspension was heated to 40° and treated with 'hyperol' (1.4 gm.). After a few minutes the

mixture was diluted to 50 cc. and heated on the steam bath till solution was complete. On acidification with dilute hydrochloric acid, the substituted naphthalic acid formed was precipitated. It was filtered, washed and dried. Yield, 1 gm. On recrystallisation from acetic anhydride, the melting-point was 227-8°. Yield, 0.6 gm. Further purification was effected by dissolving in alkali and precipitating the sodium salt of the naphthalic acid with sodium chloride. The acid liberated from the sodium salt was subsequently recrystallised from acetic anhydride, the melting point of the compound being then raised to 230-231°. When mixed with the tribromo-naphthalic anhydride of melting point 232°, already obtained by the direct bromination of naphthalic anhydride, it melted at 231-232°.

IV (B) Further Substitution of Mono-substituted Derivatives of Naphthalic Anhydride. Nitration of 4-Bromo- and 4-Nitro-Naphthalic Anhydrides.

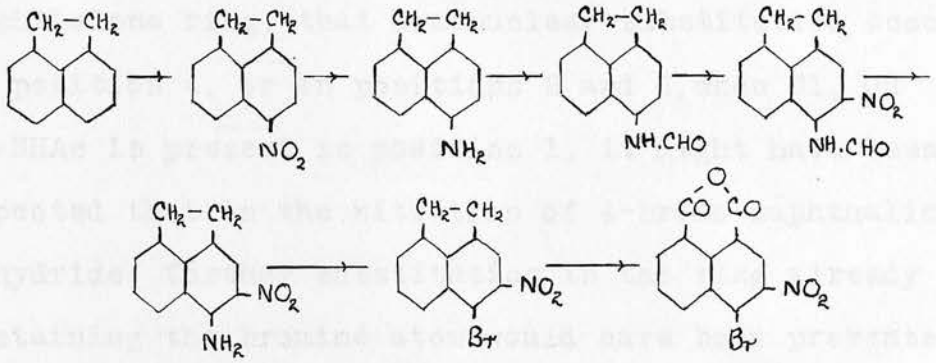
Attention has already been drawn (General Introduction, p. 16) to the fact that the introduction of a second substituent into mono-substituted derivatives of naphthalic anhydride has not been extensively investigated, though it has been shown that 3-nitro-naphthalic anhydride gives the 3:6-dinitro-compound on further nitration (Rule and Brown, J. Chem. Soc., 1934, 171) whilst by nitration of 2-methoxy-naphthalic anhydride, 2-methoxy-6-nitro-naphthalic anhydride results (Davies, Heilbron and Irving, J. Chem. Soc., 1932, 2715). In the course of the present work 4-bromo- and 4-nitro-naphthalic anhydrides have been mononitrated and the orientation of the derivatives established in each case.

In the nitration of 4-bromo-naphthalic anhydride three possible products may be looked for:



Of these I is excluded as it has already been prepared by Dziewonski, Schoen, and Glazner (Bull. inter. acad. polon., 1929 A, 636) and is stated to melt at

312°, whereas the compound at present obtained melted at 232°. It remained to decide between formulae II and III. This was accomplished by direct comparison with a specimen of III, synthesised by the following series of reactions which show its constitution. The stages up to the formation of 3-nitro-4-amino-acenaphthene have already been carried out by Morgan and his co-workers (J. Soc. Chem. Ind., 1924, 343T; 1925, 493T; 1930, 413T)

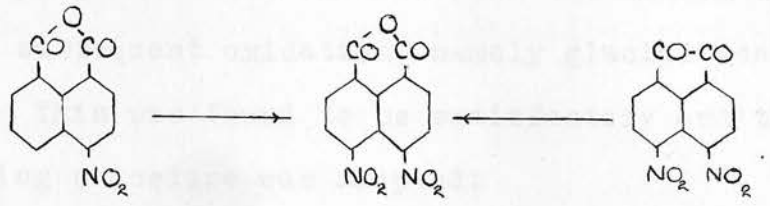


Identity of the 3-nitro-4-bromo-naphthalic anhydride thus prepared with the product from the nitration of 4-bromo-naphthalic anhydride was established.

This result is perhaps rather surprising in view of our knowledge of the general influence of substituents on further substitution in the benzene nucleus. (cf. Francis, Chem. Rev., 1927, 3, 277) Though Hollemann has stated that the rate of ortho- and para-substitution is much greater than that of meta-substitution, evidence in contradiction of this rule has been produced when the substituent is a halogen atom. Thus bromine attacks chlorobenzene much more

slowly than it does benzene itself. Also experiments by Olivier on the hydrolysis of substituted benzyl chlorides (discussed by Francis, loc. cit.) lead to the conclusion that halogens exert a retarding effect, resembling in this respect the meta- rather than the o- p- directing groups. Thus, though Wynne (Article on Naphthalene, Thorpe's Dictionary of Applied Chemistry (1922), p. 414) states, as a generalisation with regard to further substitution in the naphthalene ring, that homonuclear substitution occurs in position 4, or in positions 2 and 4, when Cl, OH or NHAc is present in position 1, it might have been expected that in the nitration of 4-bromo-naphthalic anhydride, further substitution in the ring already containing the bromine atom would have been prevented. The experimental results however show that 3-nitro-4-bromo-naphthalic anhydride is formed predominantly.

On the other hand by the nitration of 4-nitro-naphthalic anhydride, 4:5-dinitro-naphthalic anhydride was obtained. The identity of the product was proved by comparison with that obtained by oxidation of 4:5-dinitro-acenaphthenequinone, the work of Rule and Brown (loc. cit.) having more definitely established the constitution ascribed to this compound by Rowe and Davies (J. Chem. Soc., 1920, 1344) and Mayer and Kaufmann (Ber., 1920, 53, 289).



There thus appears to be some evidence indicating that a nitro-group in one peri-position tends to direct a second nitro-group into the adjacent peri-position thus bringing out an analogy between the peri-positions and the meta-positions in the benzene ring.

Experimental

Preparation of 4-Bromo-naphthalic Anhydride.

Several methods for the preparation of this compound are available. The oxidation of 4-bromo-acenaphthenequinone as already described (p. 29) could now be conveniently applied on a larger scale, while the direct bromination of naphthalic acid described on p. 49 might also be employed. It was considered however that oxidation of 4-bromo-acenaphthene would probably provide the cheapest and most efficient method, though yields from this reaction are not recorded in the literature. While bromination of acenaphthene has hitherto been carried out either in chloroform or ether solution, it was also thought that much time and trouble involved in its isolation under these circumstances might be obviated

by carrying out the bromination in the medium used in the subsequent oxidation, namely glacial acetic acid. This was found to be satisfactory and the following procedure was adopted:

Acenaphthene (50 gm.) was dissolved in 200 cc. of glacial acetic acid heated to the boiling-point in a flask fitted with a reflux condenser , and bromine (18 cc. dissolved in 50 cc. of glacial acetic acid) dropped in gradually. Boiling was continued till most of the hydrogen bromide was removed. The contents of the flask were transferred to a large beaker, the flask being washed out with a further 150 cc. of glacial acetic acid. The oxidation was then carried out as described by Graebe and Guinsberg (Ann., 1903, 327, 87), 250 gm. of coarsely powdered sodium dichromate being added gradually to the solution, at 50°, care being taken not to allow the reaction to become too vigorous. After the addition the mixture was warmed on a water bath for half-an-hour and then boiled under reflux for two hours. The bromo-acid was obtained by pouring into water, and extracting the precipitated product with sodium carbonate solution. The filtrate on acidification gave 40 gm. of the crude compound which on recrystallisation from acetic acid melted at 212-215°. Yield, 32 gm. (35% of theoretical calculated on weight of acenaphthene used) Acetic anhydride, glacial acetic acid

and nitrobenzene are convenient solvents for the recrystallisation of 4-bromo-naphthalic anhydride.

Nitration of 4-Bromo-naphthalic anhydride.

3 gm. 4-bromo-naphthalic anhydride

20 cc. concentrated sulphuric acid

Nitrating acid - 0.50 cc. fuming nitric acid (d, 1.51) in 10 cc. concentrated sulphuric acid.

The bromo-naphthalic anhydride was dissolved in the sulphuric acid and the nitrating acid dropped in gradually with constant shaking at 15-20°. The mixture was heated for one hour on a boiling water bath and then poured into a large volume of water. The precipitated nitro-compound was filtered, washed well and dried. After two recrystallisations from acetic anhydride the product melted at 229-230°. Yield, 1.4 gm. (40% of theoretical). A further recrystallisation from concentrated nitric acid raised the melting point to 231-2°, this figure being unaffected by further treatment. The compound was obtained as fine, white needles.

Analysis by micro-Dumas method.

Found: N, 4.5.

Calculated for $C_{12}H_4O_5NBr$: N, 4.35%

Preparation of 3-nitro-4-bromo-naphthalic anhydride.

Ref.- The stages in this preparation up to the diązotisation of 3-nitro-4-amino-acenaphthene are described in the following papers -

Morgan and Stanley, J. Soc. Chem. Ind., 1924, 343T, 1925, 493T.

Morgan and Harrison, ibid, 1930, 413T.

Nitration of acenaphthene: Acenaphthene (100 gm.) was heated with 600 cc. of glacial acetic acid till solution was complete. The solution was cooled to 10° and 100 cc. of concentrated nitric acid (d, 1.41) added gradually with stirring and cooling. During the first half of the addition the temperature was not allowed to rise above 15°, but the cooling bath was removed before the rest of the acid was dropped in, when the temperature rose to 25-30°. Stirring was continued for some time and the mixture was then allowed to stand overnight. The nitro-compound was filtered off and washed first with a little glacial acetic acid and then with water.

Reduction of 4-nitro-acenaphthene: The nitro-compound as prepared above was dissolved in a litre of alcohol to which 500 cc. of water had been added. To the hot solution 350 gm. of sodium hydrosulphite were added in three portions. The mixture was boiled under reflux till the foam became colourless, when the alcohol was distilled off. The amine was extracted from the residue with hydrochloric acid, the filtrates being made alkaline with ammonia. After allowing to stand overnight in a cool place the

4-amino-acenaphthene was filtered off. It was recrystallised from petrol ether (b.p., 80-100°).

Preparation of 4-formyl-amino-acenaphthene: 4-Amino-acenaphthene (25 gm.) was boiled under reflux with 100 cc. of 90% formic acid for one hour, the formyl derivative being precipitated on pouring into water.

Nitration of 4-formyl-amino-acenaphthene: 4-Formyl-amino-acenaphthene (25 gm.) was dissolved by warming with 100 cc. of glacial acetic acid, the solution being then cooled to 10°. Nitric acid (30 cc. of d, 1.41) was dropped in gradually, the temperature not being allowed to exceed 15°. Stirring was continued for some time, the mixture being then allowed to stand overnight. The nitro-compound was filtered off, washed first with glacial acetic acid and then with water and dried. Yield, 75% of theory.

Preparation of 3-nitro-4-amino-acenaphthene: 10 gm. of the formyl-amino derivative were heated under reflux with 150 cc. of alcohol and 20 cc. of concentrated hydrochloric acid. Boiling was continued for 30 minutes, the amine separating from the solution on cooling. Yield, 8.6 gm. (nearly theoretical) M.p. 219°.

Preparation of 3-nitro-4-bromo-acenaphthene: 3-Nitro-4-amino-acenaphthene (5 gm.) was added gradually with stirring to 40 cc. of 85% sulphuric acid, and 50 cc. of glacial acetic acid were added to the resulting suspension, when a clear solution was obtained. To the well-cooled and stirred solution 3.5 gm. of finely

powdered sodium nitrite and 200 gm. of ice were added successively.

Cuprous bromide (10 gm.) was dissolved in 100 cc. of 39% hydrobromic acid and 100 cc. of water. The diazo-solution was poured into this solution, evolution of nitrogen immediately taking place. The temperature was raised gradually to 60°, the mixture being efficiently stirred. After allowing to stand overnight at room temperature the solid was filtered off (weight, 6 gm.) and extracted in a modified Soxhlet apparatus with petrol ether (b.p. 80-100°). On cooling, orange coloured crystals of m.p. 130-135° separated. Weight, 2.5 gm. The product could be recrystallised from petrol ether or from alcohol, the melting point of the pure compound being 143°. Under the microscope it appeared as long, rectangular prisms.

Analysis. Found: Br, 29.1.

Calculated for $C_{12}H_8O_2NBr$: Br, 28.8%.

Oxidation of 3-nitro-4-bromo-acenaphthene.

Some trouble was experienced at this stage, the desired compound not being isolated when too vigorous conditions of oxidation were employed, namely on boiling with sodium dichromate and glacial acetic acid. The following procedure was satisfactory however:-

3-Nitro-4-bromo-acenaphthene (2 gm. of m.p.

130-135°) was dissolved in 25 cc. of glacial acetic acid by heating to 70-80°. Coarsely powdered dry sodium dichromate (10 gm.) was added gradually. When the addition was complete the mixture was heated on a boiling water-bath for half-an-hour. It was then poured into water acidified with dilute sulphuric acid, and filtered after standing for some time. The product was washed well with water and extracted with sodium carbonate solution. There remained undissolved an orange-coloured residue, which resisted oxidation under more vigorous conditions, dissolved sparingly in glacial acetic acid and did not melt below 360°. From the carbonate extract on acidification a slightly brownish coloured product was obtained. On recrystallisation from concentrated nitric acid the latter formed fine needles, which melted sharply at 232°. Yield, 0.4 gm. Further recrystallisation did not change this melting point.

A mixed melting point with the compound, m.p. 231-2°, obtained by nitration of 4-bromo-naphthalic anhydride showed no depression. The latter product is therefore proved to be 3-nitro-4-bromo-naphthalic anhydride. In accordance with this assumption it was found that the compounds from both sources agreed in their solubility properties. Recrystallisation could be readily carried out from acetic anhydride, glacial acetic acid or concentrated nitric acid.

Moreover, the product from the latter solvent in each case presented the same appearance under the microscope, the crystals being in the form of long, slender needles.

Preparation of 4-nitro-naphthalic anhydride.

Nitro-acenaphthene (20 gm.) was dissolved by heating with 250 cc. of glacial acetic acid in a large beaker. Coarsely powdered dry sodium dichromate (140 gm.) was added gradually to the solution at 50°, the temperature in the course of the addition being kept below 80°. The mixture was then heated for three hours on the steam bath and poured into water acidified with sulphuric acid. The product, after filtering and washing, was extracted with a boiling solution of sodium carbonate (10 gm. in 1½ litres of water). The hot filtrate on acidification yielded the nitro-naphthalic acid, a further small quantity being obtained by a second extraction. Yield, 15 gm. M.p. 229-230°.

Nitration of 4-nitro-naphthalic anhydride.

5 gm. 4-nitro-naphthalic anhydride

30 cc. concentrated sulphuric acid

2 gm. sodium nitrate.

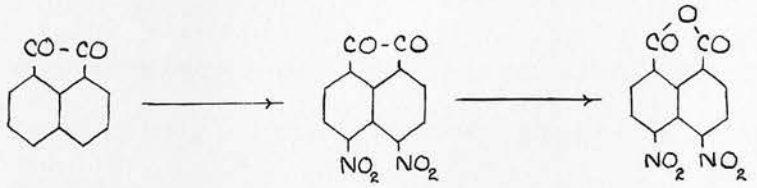
The nitro-naphthalic anhydride was introduced gradually with shaking into the sulphuric acid, and the finely powdered sodium nitrate added slowly with con-

stant shaking at room temperature. The temperature of the mixture was then raised gradually on a water-bath to 100°. After a few minutes crystals began to separate from the warm sulphuric acid solution and soon a pasty magma formed. Heating was continued for 15 minutes, and the mixture allowed to cool. It was filtered through a sintered glass crucible, and washed first with a little cold sulphuric acid and then with water. Yield, 2.2 gm. M.p. 320-322°. The compound could be conveniently recrystallised from concentrated nitric acid when the melting point was raised to 323-5°.

Instead of allowing crystallisation from the reaction mixture to take place, the product could be poured into water and purified by recrystallisations from acetic acid, nitric acid, or nitrobenzene, the final yield being slightly less than by the above procedure.

Preparation of 4:5-dinitro-naphthalic anhydride.

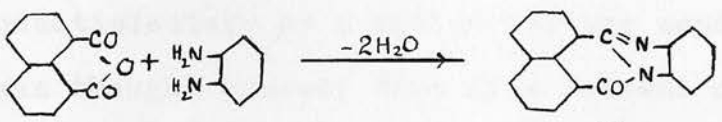
Acenaphthenequinone was dinitrated and the product oxidised to the corresponding naphthalic anhydride. (Rowe and Davies, J. Chem. Soc., 1920, 1344; Mayer and Kaufmann, Ber., 1920, 53, 289)



Since the details given in the literature were followed a full account of these preparations need not be given. It was found however that several recrystallisations of the 4:5-dinitro-naphthalic anhydride from concentrated nitric acid raised the melting point to 327-9°. (Mayer and Kaufmann record 310°.) A mixed melting point with the compound of melting point 323-5° obtained by the nitration of 4-nitro-naphthalic anhydride gave the figure 326-8°. It follows that the latter is 4:5-dinitro-naphthalic anhydride. The microscopic appearance was the same in each case, the crystals obtained from concentrated nitric acid being in the form of elongated, rectangular plates.

V. THE REACTION BETWEEN o-PHENYLENEDIAMINE AND NAPHTHALIC ANHYDRIDE AND ITS SUBSTITUTED DERIVATIVES.

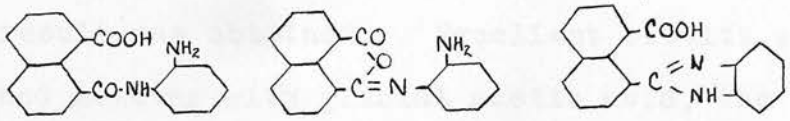
The condensation in alcoholic solution of naphthalic anhydride and o-phenylene diamine has been investigated by Chakravarti (J. Ind. Chem. Soc., 1924, 1, 19) and by Bistrzycki and Risi (Helv. Chim. Acta, 1925, 8, 810). The results of both investigations agree in that the final condensation product, 1:8-naphthoylene-1:2-benziminazole (I), corresponding to the loss of two molecules of water, is not under these circumstances obtained directly.



I

Bistrzycki and Risi state that an addition compound (II) is formed, which dissolves in alkali with partial

decomposition into its components. On heating for ten minutes at 150° loss of water with formation of I occurred.



II III IV

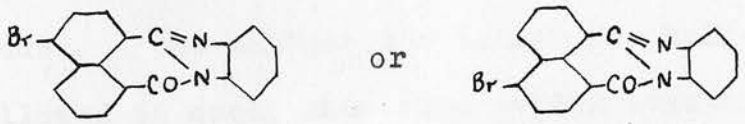
Chakravarti however gave a longer time for reaction to take place and states that he could isolate from the product o-amino-naphthalanil (III) of which an acetyl derivative could be prepared, and benziminazole-2-naphthyl-8'-carboxylic acid (IV), the separation depending on the solubility of the latter in alkali. Both of these compounds on heating at 210-220° gave I.

In the course of the present work the condensation between o-phenylenediamine and substituted naphthalic anhydrides, with loss of two molecules of water to give well-defined derivatives of the type I, was considered as a means of characterisation. Moreover such derivatives are of possible interest as dye-stuffs.

It is obvious from the above account that alcohol is unsatisfactory as a medium for the condensation. It was thought however that if a solvent of high boiling point such as nitrobenzene were used condensation would take place more readily and that the condensation products, not being readily soluble, would be obtained directly on cooling. An experiment was

carried out with naphthalic anhydride and phenylene-diamine to test this possibility but no condensation took place, unchanged naphthalic anhydride being recovered. When pyridine was used as solvent the same result was obtained. Excellent results were obtained however with glacial acetic acid, the utility of this solvent as a medium for condensation between keto- and amino- groups having already been observed in the course of the present work (c.f. preparations of phenylhydrazones and phenazines of acenaphthenequinone and its derivatives). Naphthalic anhydride and o-phenylenediamine react readily in boiling glacial acetic acid with formation of the compound I.

Extending this observation to various substituted naphthalic anhydrides results have been obtained as described below. In the case of symmetrical disubstituted derivatives - 3:6-dinitro and 4:5-dinitro naphthalic anhydrides - only one compound is possible, and well-defined derivatives were immediately obtained. When there is only one substituent, however, two isomerides are possible. Thus in the case of 4-bromo-naphthalic anhydride we may have



It appeared that mixtures were in fact formed in those cases where the substituted naphthalic anhydrides were

unsymmetrical, i.e. with 3-bromo-, 4-bromo-, 3-nitro-, 4-nitro-, and tribromo-naphthalic anhydrides.

Experimental.

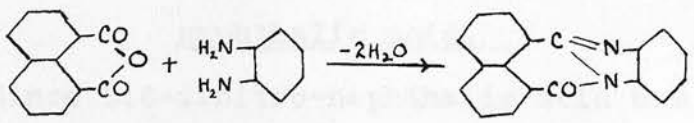
Condensation of Naphthalic Anhydride and o-Phenylenediamine.

Condensation did not take place when equimolecular quantities of the reactants were boiled in nitrobenzene or in pyridine solution for half-an-hour. On allowing to cool, part (30%) of the naphthalic anhydride used was recovered in each case, being identified by melting-point and mixed melting-point. It is possible that the naphthalic anhydride which was not recovered formed some compound with o-phenyl enediamine which was more soluble in pyridine and nitrobenzene. Obviously however a reaction of the type desired had not taken place. The condensation was successfully carried out in glacial acetic acid solution as follows:-

Naphthalic anhydride (2 gm.) was dissolved in 60 cc. glacial acetic acid, and to the boiling solution a molecular proportion of o-phenylenediamine (1.2 gm.) dissolved in 10 cc. glacial acetic acid was added. The mixture was boiled for half-an-hour, and allowed to cool, when fine yellow crystals separated. These were filtered off, washed with a little cold glacial acetic acid, and dried. Weight 2.2 gm.

M.p. 206-7°.

It was proved that no compounds of acidic nature (cf. II and IV above) were present, by boiling the product with sodium carbonate solution. The mixture was filtered, and the filtrate acidified with dilute hydrochloric acid. No precipitate was obtained. Now the melting-point recorded for o-amino-naphthalanil is 245° (Chakravarti, loc. cit.), so this also is excluded as a possible product. Clearly the condensation must have taken the course:



The compound can be recrystallised from glacial acetic acid, or more conveniently from nitrobenzene or chloro-benzene, the melting point of the pure compound being 209°. (Bistrzycki and Risi record 189° and Chakravarti 198°)

Analysis by micro-Dumas method.

Found: N, 10·3. Calculated for $C_{18}H_{10}ON_2$: N, 10·4%.

Condensation of o-phenylenediamine and 4:5-dinitro-naphthalic anhydride.

1.4 gm. 4:5-dinitronaphthalic anhydride

0.6 gm. o-phenylenediamine.

The dinitro-compound was heated to boiling in 75 cc. glacial acetic acid, and the phenylenediamine

dissolved in 10 cc. glacial acetic acid was added. The mixture was boiled gently under reflux for half-an-hour, and allowed to cool. Fine, bronze-coloured needles of the condensation compound (4:5-dinitro-1:8-naphthoylene-1:2-benziminazole) were obtained. Yield, 1.5 gm. M.p., 370°.

Analysis by micro-Dumas method.

Found: N, 15.2, 15.5.

Calculated for $C_{18}H_8O_5N_4$: N, 15.55.

Condensation of o-phenylenediamine and 3:6-dinitro-naphthalic acid.

Since 3:6-dinitro-naphthalic acid has not been prepared in connection with any other part of the present work, it was obtained for the purpose of this experiment by the method of Francesconi and Bargellini (Gazz., 1902, 32, 2, 90), this method having recently been used by Rule and Brown (J. Chem. Soc., 1934, 173) in their work on the constitution of the compound. Whilst this dinitro-acid is rather soluble in most of the common organic solvents, the workers just mentioned having recrystallised it from water, it was observed during the present work that it could be conveniently recrystallised from nitrobenzene. Naphthalic acid itself when heated in nitrobenzene solution loses water to give the anhydride, but in the present case the dinitro-compound obtained even after boiling for some time with nitrobenzene possessed the same melting point

(210° with slight softening just below that temperature) as the product obtained on recrystallisation from water. Francesconi and Bargellini (loc. cit.) state that recrystallisation from concentrated nitric acid gave the anhydride, m.p. 266° with decomposition. In the course of the present work a sample of the compound purified from nitrobenzene was recrystallised from concentrated nitric acid when long, white needles, melting at 330° without any signs of decomposition, were obtained.

Analysis by micro-Dumas method of compound of m.p. 330°.

Found: N, 9.98.

Calculated for dinitro naphthalic anhydride, $C_{12}H_4O_7N_2$: N, 9.72%.

For the condensation with o-phenylenediamine the dinitro-compound obtained by crystallisation from nitrobenzene was found to be suitable. The compound (2.8 gm.) was dissolved in 50 cc, glacial acetic acid and o-phenylenediamine (1.2 gm.) in 10 cc. of the same solvent added. A deep red coloured solution was formed from which almost immediately crystals of a fine orange colour began to separate. The reaction was completed by maintaining the mixture at the boiling point for half-an-hour. It was then allowed to cool and filtered. Yield, 3.4 gm. M.p., 301°.

Analysis by micro-Dumas method.

Found: N, 15.23.

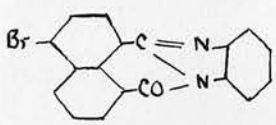
Calculated for 3:6-dinitro-1:8-naphthoylene-1:2-benziminazole, $C_{18}H_8O_5N_4$: N, 15.55%.

Condensation of o-phenylenediamine and 4-bromo-naphthalic anhydride.

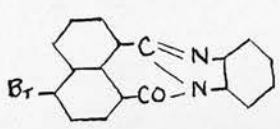
1.4 gm. 4-bromo naphthalic anhydride

0.6 gm. o-phenylenediamine.

To a solution of the 4-bromo-naphthalic anhydride in 25 cc. of boiling glacial acetic acid, the phenylene-diamine, dissolved in 10 cc. glacial acetic acid, was added. The mixture was boiled under reflux for half-an-hour, and allowed to cool. The condensation product was bright yellow in colour, and melted unsharply from 250° upwards. To determine whether condensation of the type IV (p. 88) had taken place the product was boiled with 10% sodium carbonate solution. No solution occurred however, the sodium carbonate filtrate on acidification yielding no precipitate. On washing and drying the product it melted over the same range as before. On recrystal-lisation from glacial acetic acid it melted from 250-270°. Nitrobenzene was also found to be a suitable solvent for recrystallisation, but the melting point was not raised or made more sharp when it was used. An analysis by the micro-Dumas method supports the conclusion that a mixture of the isomerides,



and



is formed.

Found: N, 8.2.

Calculated for $C_{18}H_9ON_2Br$: N, 8.02%.

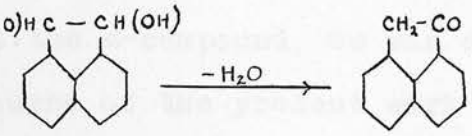
Since other unsymmetrical naphthalic anhydrides when condensed with o-phenylenediamine gave results similar to those obtained with 4-bromo-naphthalic anhydride, no fuller description need be given than is contained in the following tabular summary.

Substituent in naphthalic anhydride.	Melting point of product with o-phenylenediamine	Colour
None	209°	pale yellow
4:5-dinitro-	370°	light brown
3:6-dinitro	301°	orange
4-bromo	all mixtures melting unsharply	bright yellow
3-bromo		bright yellow
4-nitro		orange
3-nitro		orange-brown
tribromo		deep yellow

VI STUDIES ON ACENAPHTHENONE.

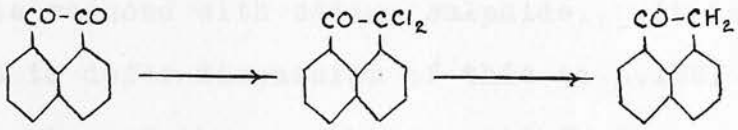
(A.) The Preparation of Acenaphthenone - Some New Methods.

This compound, of which mention has already been made (General Introduction p. 10), was first obtained by Ewan and Cohen (J. Chem. Soc., 1889, 55, 578) in an attempt to prepare the methyl derivative of acenaphthylene glycol using methyl iodide and sodium ethoxide. Instead of the expected reaction dehydration took place:



A few years later Graebe and Gfeller (Ann., 1893, 276, 1) obtained acenaphthenone more conveniently by the reduction of acenaphthenequinone with zinc dust and glacial acetic acid. The yields however were variable and rather poor, the optimum being about

35%. An improvement was effected by Graebe and Jequier (Ann., 1896, 290, 195) who made use as an intermediate of the dichloro compound (1:1'-dichloracenaphthenone) obtained by the action of phosphorus pentachloride on acenaphthenequinone. Reduction of this compound, again using zinc and glacial acetic acid, gave acenaphthenone.



The optimum yield reported for the last stage is 45%.

This has been the best method hitherto available for the preparation of acenaphthenone, and was that used by Morgan and Stanley (J. Soc. Chem. Ind., 1925, 493 T). These authors further state that a method described in the patent literature - ring closure of the condensation product of chloracetyl chloride and naphthalene (D.R.P. 230,237; C., 11, I, 359) - does not give the product claimed. They found that the primary condensation product was β-naphthyl-chloromethyl ketone and not the α-compound, as was desired.

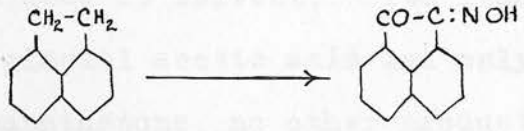
In the course of the present work acenaphthenone was first prepared by the method of Graebe and Jequier. As precise experimental details of the reduction are not given in the literature, the conditions, using zinc dust and glacial acetic acid, were systematically varied. No improvement on the recorded yield could

be obtained, and in the majority of cases the yield was considerably less. A variety of other methods, mentioned below in the experimental section, of reducing the dichloro-compound have been tried in an attempt to increase the yield, but success has not been attained in this respect. An interesting result emerges however when an alcoholic solution of the dichloro-compound is reduced with sodium sulphide. It is convenient to defer discussion of this to p.132.

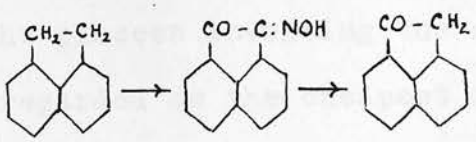
In view of the somewhat unsatisfactory nature of the above methods for the preparation of acenaphthenone attention has been directed to other possible processes. Experiments carried out with a view to adapting the results of Marquis (vide p. 10) to give a good preparative method having failed to achieve their object, the reduction of acenaphthenequinone derivatives substituted in one of the keto-groups has been considered. Of such compounds the oxime, the phenylhydrazone, the semicarbazone and the monoanil, already described in the literature, have been studied. Others such as the hydrazone (Berend and Herms, J. pr. Chem., 1899, 60, 1) and the compound with urea (Ampola and Recchi, Atti. real. accad. de Lincei, 8, 209; C., 99, II, 338) were considered unsuitable as they are not readily prepared, particularly in quantity.

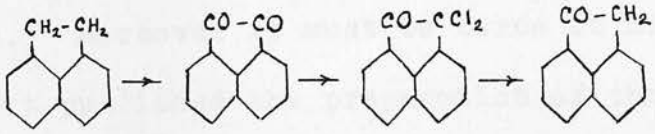
Results of value have been obtained from the examination of the oxime. In addition to its preparation by the action of hydroxylamine hydrochloride

on acenaphthenequinone in alcoholic solution (Francesconi and Pirazolli, Gazz., 1903, 33, 1, 36), a procedure which is limited to small quantities, it can be prepared on a large scale by the method of Reissert (Ber., 1911, 44, 1749) starting from acenaphthene. The hydrocarbon, in solution in amyl alcohol, is treated with amyl nitrite, while hydrogen chloride gas is passed in. In the resulting reaction oxidation of one of the methylene groups to a keto-group takes place in addition to oxime formation.



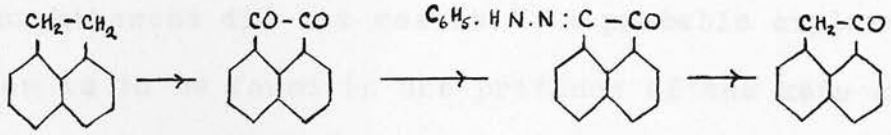
Following out the proposed scheme the reduction of the oxime has been investigated. When iron filings and 75% acetic acid constituted the reducing agent, acenaphthenone was obtained in 40% yield. This method (i) therefore shows an advance on the best method hitherto available (ii), since, regarding acenaphthene as the starting material, the desired product is reached in a smaller number of stages and the over-all yield is greater.

(i) 

(ii) 

Other methods of reduction of the oxime were tried, first with a view to improving the yield, and then in the expectation that other products of reduction, particularly the amine, might be isolated. Though success has not been attained in the latter respect, it was found that the yield was slightly improved when iron filings and a mixture of glacial acetic acid and concentrated hydrochloric acid were used.

Acenaphthenequinone phenylhydrazone can be obtained, in fairly large quantities and good yield, when glacial acetic acid is used as solvent. Its reduction with zinc dust and glacial acetic acid led only to a small amount of acenaphthenone, no other product being isolated. When, however, iron filings and glacial acetic acid containing 25% concentrated hydrochloric acid were used quite a good yield was obtained (50 %). The following series of reactions therefore constitutes another serviceable method for the preparation of acenaphthenone.



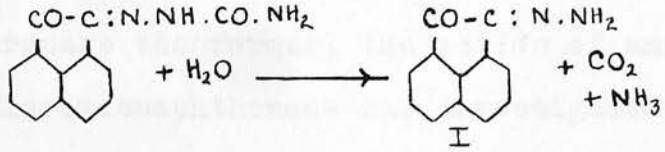
The process involving the oxime is however still to be regarded as the cheapest and best. Starting from acenaphthene it involves a smaller number of stages. Moreover it must be borne in mind that Reissert published the preparation of the oxime with

its subsequent hydrolysis as a method of preparing acenaphthenequinone, and that, whilst the direct oxidation of acenaphthene under the conditions described by Graebe is generally accepted for that purpose, this is not invariably the case. Thus de Fazi (Gazz., 1924, 54, 658) preferred Reissert's method because though longer it gave better yields. It is obvious therefore that the oxime is much more readily accessible than the phenylhydrazone.

Although the semicarbazone is not readily prepared in large quantities, it is of interest in that the applicability of the general method of Wolff (Ann., 1912, 394, 86) for the replacement of the oxygen of ketones or aldehydes by hydrogen may be tested. This involves the treatment of the semicarbazone with sodium hydroxide or sodium ethoxide in a sealed tube. Whilst in the case of the disemicarbazone of acenaphthenequinone, acenaphthene has been obtained by this method (Schonberg, Ber., 1921, 54, 2838) in the present case acenaphthenone did not result. A probable explanation is to be found in the presence of the keto group which is likely to undergo condensation reactions, a compound of melting point 305° , the constitution of which has not been definitely proved, having been isolated.

The first stage in this reaction probably involves loss of carbon dioxide and ammonia (cf. Wolff, loc. cit.)

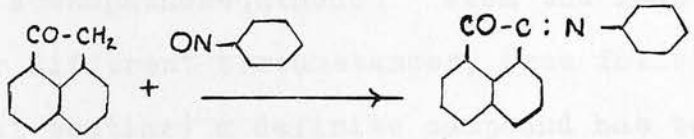
water playing an important part according to the equation:



I

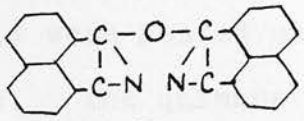
The hydrazone (I) will react further, either internal condensation, or condensation between two molecules taking place, the condensation in either event probably being followed by reduction. In both cases there is agreement in the nitrogen content of the product with that found by analysis.

Though the anil of acenaphthenequinone is described in the literature (Sander, Ber., 1925, 58, 830), the method of preparation given involves the use of acenaphthenone itself, condensation with nitrosobenzene being effected.

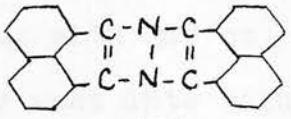


No record of any investigation of the direct reaction between aniline and acenaphthenequinone having been found in the literature a study of this has now been made. By careful treatment with slight excess of the molecular quantity of aniline at 130°C a monoanil has been obtained.

As the imide and methyl imide of acenaphthenequinone are unknown attempts have been made to prepare them in the course of the present work. In an attempt to prepare the former, the action of ammonia on 1:1'-dichloroacenaphthenone was investigated. A red compound of very high melting point, which has been identified with the product of interaction of ammonia and acenaphthenequinone, was isolated. Graebe (Ann., 1893, 276, 9) originally assigned the formula I to this compound, but Schonberg and Nedzati (Ber., 1921, 54, 238) have since produced strong evidence for an azine structure (II).



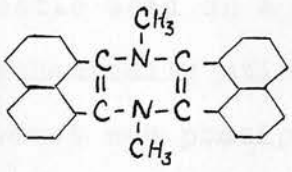
I



II

Methylamine in aqueous solution reacts readily with acenaphthenequinone. From the reaction mixture, under different circumstances, (see following experimental section) a definite compound has been isolated. This is brown in colour, and resembles the compound with ammonia which has just been described in possessing a very high melting point and being soluble with difficulty in the common organic solvents. It can be recrystallised from a relatively large volume of nitrobenzene, when it forms beautiful brown crystals. As it is probable that the compound will possess a structure similar to that of the compound obtained by

reaction with ammonia, it may be formulated as III, the results of analysis agreeing with this.



III

Experimental

PREPARATION OF ACENAPHTHENONE.

Method (a)

Refs.- Graebe and Jequier, Ann., 1896, 290, 195.
Morgan and Stanley, J. Soc. Chem. Ind., 1925, 493 T.

Preparation of 1:1'-dichloroacenaphthenone: Acenaphthenequinone (50 gm.) and phosphorus pentachloride (59.gm.) were heated under reflux with 200 cc. of toluene. The quinone gradually went into solution, the reaction being considered complete at the end of 1 hour. The mixture was filtered hot and the filtrate diluted with petrol ether (b.p. 40-60°). The crude dichloroacenaphthenone (yield, 53 gm.) is suitable for the next stage in the preparation. It can be purified by warming with sodium bisulphite and recrystallising from benzene. M.p. 146°.

It was thought that thionyl chloride might conveniently be employed in the preparation of the dichloro-compound, but, after boiling under reflux with excess of thionyl chloride for an hour, acenaphthenequinone was recovered unchanged.

Reduction: The best result in the reduction was

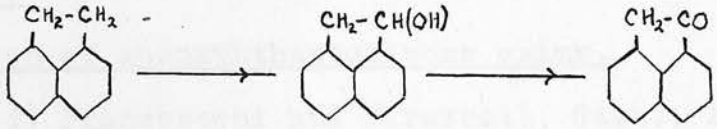
obtained by the following procedure: Zinc dust (15 gm.) was added gradually to 10 gm. of the dichloro-compound in 40 cc. glacial acetic acid on a water bath at 90°, the mixture being mechanically stirred. At the end of two hours the product was precipitated by pouring into water and isolated by steam distillation. Yield, 2.3 gm. (32% of theoretical). M.p., 121°.

Attempts to reduce the dichloro-compound by means of hydrogen in boiling toluene in presence of a little palladium as catalyst, by copper in sulphuric acid at 0°, and by tin and hydrochloric acid led to no favourable results.

Method (b)

Oxidation of acenaphthene to acenaphthenone.

(Ref. - Marquis, Compt. rend., 1926, 182, 1227.)



Acenaphthene (10 gm.) was dissolved in 50 cc. glacial acetic acid and lead dioxide (17 gm.) added gradually to the solution, heated to 50°C, in the course of one hour. The temperature was allowed to rise to

80° and maintained at that figure for a further hour. On pouring into water a semi-solid product separated, containing acenaphthenol and its acetate, together with resinous by-products of the reaction and some unchanged acenaphthene. This was boiled for a short time with alcoholic potassium hydroxide, poured into water, filtered off and dried. The tarry substance obtained was dissolved in 50 cc. glacial acetic acid and heated to 40°. Finely powdered dry sodium dichromate (10 gm.) was added gradually with stirring. When reaction was seen to be complete, the mixture was poured into water and steam distilled. The acenaphthenone which passed over contained a yellow substance - probably acenaphthylene - as impurity. Yield, 0.9 gm., less than 10% of the theoretical.

Method (c)

Preparation of acenaphthenequinone oxime.

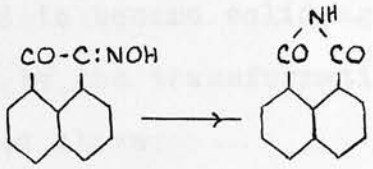
Refs. - (i) Francesconi and Pirazzoli, Gazz., 1903, 33, [1], 36.

(ii) Reissert, Ber., 1911, 44, 1749.

(i) A solution of hydroxylamine hydrochloride (0.8 gm.) was added to a boiling solution of acenaphthenequinone (2 gm.) in 500 cc. of 95% alcohol. The colour of the solution deepens from yellow to orange. The mixture

was boiled under reflux for half-an-hour and about 400 cc. of the alcohol then distilled off through a condenser. Boiling water was added to the solution till a faint turbidity appeared. It was then allowed to crystallise. Yield, 2.1 gm. M.p., 215-219°. Recrystallisation from 60% alcohol raised the melting point to 225-227°.

The melting point is never quite sharp as the oxime decomposes on heating. This decomposition occurs rapidly when a small quantity in a test-tube is placed in an oil bath at 250°C. Needles of a sublimate appear on the upper walls of the tube. The sublimed substance was found to melt at 298°, and was proved by a mixed melting point to be naphthalimide (m.p., 300°).



(ii) 50 gm. acenaphthene
250 cc. amyl alcohol
150 gm. amyl nitrite.

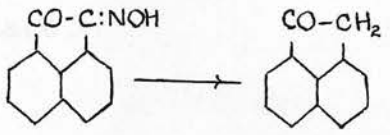
A 500 cc. flask was fitted with a cork carrying a dropping-funnel, an inlet tube for gas and a reflux condenser. The acenaphthene was dissolved in the amyl alcohol by heating the liquid to boiling point. While a constant stream of dry hydrogen chloride gas was passed in, the amyl nitrite was added in the course

of an hour, the tube of the dropping-funnel leading nearly to the bottom of the flask. After the addition the reaction was completed by boiling for a further fifteen minutes. The amyl alcohol and some unchanged acenaphthene were distilled off in steam and the solid residue triturated with dilute sodium hydroxide solution so long as this continued to take it up. A red insoluble semi-solid residue remained on filtering through asbestos fibre on a Buchner funnel. The filtrate was made faintly acid with acetic acid, when the oxime was precipitated as a yellow mass. After standing for a time this was filtered off, washed thoroughly and dried. Yield, 40 gm. When heated gradually the product showed signs of melting at 230°, but appeared to become solid again. This is readily explained by the transformation into naphthalimide described above.

Reissert (loc. cit.) claims to have isolated an isomeric oxime which is less soluble in sodium carbonate than that prepared in (a). In the present case it was found that the product was completely soluble in dilute sodium carbonate. Since in the preparation described by Reissert the alkaline solution of the oxime was boiled with animal charcoal, it was thought that this procedure might have effected a transformation. Experiments in which this was done, and in which precipitation was carried out with carbon dioxide instead of

acetic acid, were therefore carried out, but Reissert's observations could not be repeated.

Reduction of oxime.



Various reductions using zinc and glacial acetic acid were carried out and gave reasonable yields of acenaphthenone. Iron filings and acetic acid (75%) gave a yield of almost 40% but the following procedure was found to give the best result:-

The oxime (10 gm.) as prepared by the method of Reissert was dissolved by heating to the boiling point in a mixture of 75 cc. glacial acetic acid and 25 cc. concentrated hydrochloric acid. Iron filings (10 gm.) were then added gradually, care being taken that the reaction did not become too vigorous. When the addition was complete, the mixture was heated to the boiling point for one hour under reflux. On pouring into water and distilling in steam, acenaphthenone passed over in a pure state. Yield, 3.5 gm. (over 40% of theoretical). M.p., 121°.

A number of attempts were made to obtain other products from the reduction particularly the unknown amine, 1-amino-acenaphthenone. The methods employed included those using stannous chloride and concentrated hydrochloric acid in alcoholic solution, sodium hydrosulphite in aqueous alcoholic solution, and zinc dust

in an alkaline solution of the oxime. Electrolytic reduction was also tried. In no case could a recognisable product be isolated, complex condensation reactions apparently taking place.

Method (d)

Preparation of acenaphthenequinone phenylhydrazone.

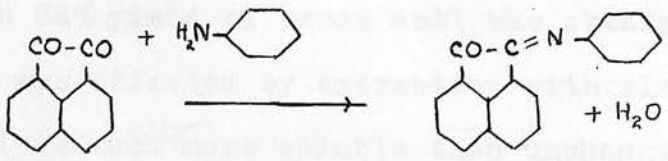
Acenaphthenequinone (15 gm.) was dissolved in the minimum (about 450 cc.) of boiling glacial acetic acid. Phenylhydrazine (10 cc.) dissolved in glacial acetic acid (50 cc.) was added to the hot solution. The mixture was then allowed to cool, when well-formed, red needles of the phenylhydrazone crystallised out. These were filtered off, washed with a little cold glacial acetic acid and dried. The pure product was obtained in this way without further recrystallisation. Yield, 20 gm. (almost 90%). M.p., 179°.

Reduction to acenaphthenone.

Acenaphthenequinone phenylhydrazone (10 gm.) was heated to the boiling point in a mixture of glacial acetic acid (75 cc.) and concentrated hydrochloric acid (25 cc.). Iron filings (10 gm.) were added cautiously, vigorous reaction taking place at each addition. After the complete addition, boiling under reflux was continued for one hour. The reaction mixture was poured into water, and the acenaphtheneone distilled over in

steam. Yield, 3.1 gm. (50% of theoretical)

Preparation of acenaphthenequinone-anil.



5 gm, acenaphthenequinone

3 cc. aniline.

The reactants were intimately mixed and heated on an oil bath at 130°. Complete melting occurred and water vapour was given off. In a few minutes the melt, which was stirred throughout the reaction, resolidified and no more water vapour was given off. The product was extracted with boiling alcohol (150 cc.) and allowed to crystallise. It was obtained as yellow needles of melting point 195-6°. Yield, 5 gm. Evaporation gave a further gram of product but this was impure, melting about 180°.

The anil could be conveniently recrystallised from alcohol or ligroin. M.p., 197-8°.

Analysis by micro-Dumas method.

Found: N, 5.55. Calculated for $C_{18}H_{11}ON$: N, 5.45%.

The use of nitrobenzene as a solvent for the above reaction was investigated. Acenaphthenequinone

was heated with four times its weight of nitrobenzene to 130°, and slight excess of the molecular quantity of aniline added with stirring in the course of half-an-hour. Heating was continued for a further one and a half hours. On distilling off the nitrobenzene in steam an 84% yield of crude anil was obtained. Purification was effected by extraction with alcohol in which the anil is much more soluble than unchanged acenaphthenequinone.

Reduction with zinc and acetic acid gave some acenaphthenone, but since this as a preparative method is unlikely to supersede the reduction of the oxime, or even the phenylhydrazone, it has not been fully investigated.

Preparation of acenaphthenequinone semicarbazone.

Ref.- Francesconi and Pirazolli, Gazz., 1903, 33, 1, 36.

Acenaphthenequinone (4 gm.) was partially dissolved in 350 cc. 95% alcohol. To the boiling mixture semicarbazide hydrochloride (2.4 gm.) dissolved in 50 cc. water was added, and boiling continued for one hour. Some undissolved acenaphthenequinone went into solution in the course of this time. Most of the alcohol was distilled off, and cooling allowed to take place. The semicarbazone was obtained as small yellow crystals of melting-point 192-193°.

Action of alcoholic sodium hydroxide on Acenaphthenequinone semicarbazone.

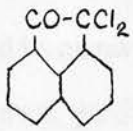
(cf. Wolff, Ann., 1912, 394, 86 - Methode zum Ersatz

des Sauerstoffatoms der Ketone und Aldehyde durch Wasserstoff)

Acenaphthenequinone semicarbazone (3 gm.) was heated for 18 hours in a sealed tube at 150° with sodium hydroxide (1 gm.) in 10 cc. alcohol and 5 cc. water. The product was acidified with dilute hydrochloric acid and steam led in. No acenaphthenone passed over. The residue was filtered off, and after washing with water, it was dried and twice recrystallised from glacial acetic acid. A brownish yellow compound, which did not melt below 300°, was obtained. On recrystallisation from nitrobenzene it formed felted crystals, coloured yellow with a faint greenish tinge. M.p., 305°C. The compound being insoluble in ether, traces of nitrobenzene could be removed by washing with this solvent.

Analysis by micro-Dumas method. Found: N, 15.1. The probable nature of the compound has already been discussed (p.101).

The action of ammonia on 1:1'-dichloroacenaphthenone:



In a preliminary experiment the dichloro-compound

(1 gm.) was boiled with concentrated aqueous ammonia in a beaker, boiling being continued for three hours with the addition of fresh ammonia from time to time. A red flocculent product was formed and this was filtered off, washed well with water and dried. An elements test (sodium fusion) showed the presence of both nitrogen and chlorine. The product melted very unsharply, and incompletely. Solubility tests showed that the red compound was insoluble in most of the common organic solvents. It could however be recrystallised from chloroform. Brilliant red needles were obtained which did not melt below 360°. An elements test on this purified product showed that nitrogen was present but chlorine absent. In addition to chloroform, nitrobenzene was found to be a suitable solvent for recrystallisation. On heating strongly in a small hard glass test-tube the compound sublimed in fine red needles.

Since it was noted that a red compound is also formed when acenaphthenequinone itself is boiled with ammonia, a search of the literature for previous work on this reaction was made. The reaction was first observed by Graebe (Ann., 1893, 276, 9), but a more complete investigation has been made by Schoenberg and Nedzati (Ber., 1921, 54, 328). Acceptable evidence for formulating the product as diacenaphthylene azotide (= acenaphthazine) has been produced by the latter workers.

The preparation of this compound has been repeated according to the directions given in the literature, and it has been found to be identical in all respects with that obtained by the action of ammonia on dichloroacenaphthenone. The solubilities are the same, and both give a red-brown colour with concentrated sulphuric acid. The most remarkable properties however are the high melting point and great stability. No change is effected on subliming with iron filings, and indeed this was found by Schoenberg and Nedzati to be a good method of obtaining the pure compound. In the course of the present work preparations both from acenaphthenequinone and the dichloro compound were submitted to this treatment, and the appearance of the product - fine, long red needles - was the same in each case.

The compound was conveniently prepared from 1:1-dichloroacenaphthenone as follows:-

5 gm. dichloroacenaphthenone

20 cc. concentrated ammonia solution

(d = .880)

The reactants were placed in a stout glass bottle with a wired-on stopper, and heated for 3-4 hours in a boiling water bath. The product was filtered off, washed with water, alcohol and ether, and dried. On recrystallisation from 50 cc. nitrobenzene red needles (2 gm.) of the acenaphthazine were obtained.

The Action of Methylamine on Acenaphthenequinone.

4.5 gm. acenaphthenequinone

3 cc. methylamine solution (30% W/V)

The methylamine solution was placed in a small test-tube which was introduced into a Carius tube and covered with a plug of glass wool. The acenaphthenequinone was placed on top of this, and the tube, after sealing, was heated for six hours at 100°. The black mass formed was removed from the tube filtered, washed and dried. It was found that acetone and chloroform in the cold removed the tarry by-products and left undissolved a light-brown, amorphous substance. This was insoluble in all the common organic solvents. It could however be recrystallised from nitrobenzene, about 100 cc. of the solvent being suitable for recrystallisation of 1 gm. of the product. Large dark-brown crystals were obtained on slow cooling. Sublimation of a small quantity gave reddish-brown needles. M.p., above 360°.

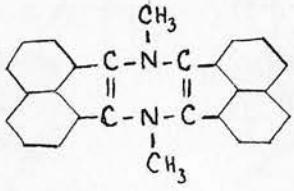
The reaction between acenaphthenequinone and methylamine also takes place in the cold though more slowly. Again black tarry by-products are formed. A number of experiments were carried out on the reaction of methylamine hydrochloride on acenaphthene-

quinone in nitrobenzene solution in presence of either sodium acetate or potassium carbonate. No satisfactory results were obtained however, much tarring taking place and only small amounts of the brown compound above described being isolated.

Analysis by micro-Dumas method.

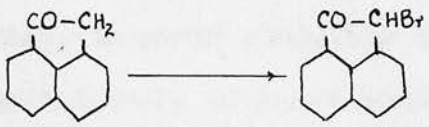
Found: N, 7.99.

Calculated for $C_{26}H_{18}N_2$: N, 7.82%.

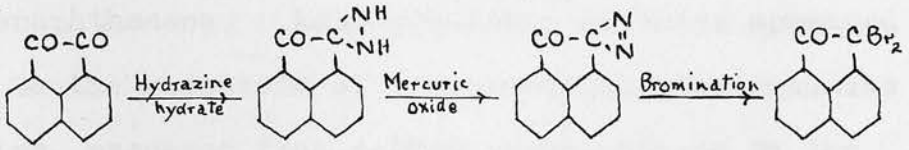


V (B) Bromine Derivatives of Acenaphthenone.

Graebe and Jequier (Ann., 1896, 290, 195) found that bromination of acenaphthenone with one molecular proportion of bromine in carbon disulphide solution gave 1-bromoacenaphthenone.



In the course of the present work the bromination has been shown to go further when excess of bromine is used. The resulting compound coincides in melting point with the 1:1-dibromoacenaphthenone obtained indirectly by Berend and Herms (J. pr. Chem., 1899, 60, 1) by the following series of reactions:



The reactivity of the methylene group thus apparently excludes the direct preparation of nuclear substituted bromine derivatives of acenaphthenone. It was thought that an interesting and hitherto unknown compound, corresponding to an oxidation product intermediate between acenaphthenone and acenaphthenequinone

might be prepared from 1-bromo-acenaphthenone by replacement of the bromine atom by a hydroxyl group, but success has not been attained in this respect. With sodium ethylate, under conditions described for the analagous preparation of benzoin from desyl bromide (Jenkins, J. Amer.Chem. Soc., 1934, 56, 682), loss of hydrogen bromide occurs with condensation between two molecules to give biacenaphthylidenedione. Shaking with moist silver oxide also failed to effect the desired change, a small quantity of biacenaphthylidenedione being the only product obtained.

As has been mentioned in the general introduction (p. 19) 4-bromo-acenaphthenone has previously been prepared by an indirect and somewhat lengthy method. The present work on the preparation of acenaphthenone which has already been described opened up, however, the possibility of other and simpler methods of approach to nuclear-substituted bromo-derivatives of acenaphthenone. Most promising of these appeared to be the reduction of 4-bromo-acenaphthenequinone oxime, prepared from 4-bromo-acenaphthene by the reaction applied by Reissert to the unsubstituted hydrocarbon (cf. p. 99), namely by the action of amyl nitrite in presence of hydrogen chloride, amyl alcohol being employed as solvent. Unexpectedly however the reaction was unsuccessful when extended

to the bromo-derivative. Only a very small quantity of a compound of oxime nature was obtained and much of the bromo-acenaphthene could be recovered unchanged. With a view to determining whether a nitro-group would have the same adverse effect on the oxime formation, 4-nitro-acenaphthene was also employed. It was found that the product contained no compound soluble in sodium hydroxide, and consisted of unchanged nitro-acenaphthene. In both cases precisely the same conditions as for acenaphthene itself were employed, with appropriate modification of the amount of amyl nitrite, and accordingly no more detailed account of the experimental procedure is given below.

When 4-bromo-acenaphthenequinone was reduced using zinc dust and glacial acetic acid, a small amount of a product sparingly volatile in steam was isolated. As thus obtained it was not however a pure substance, and after several recrystallisations the quantity obtained did not warrant further investigation, the melting point indicating however that 4-bromo-acenaphthenone (cf. p. 19) was isolated.

Experimental

Monobromination of acenaphthenone.

5 gm. acenaphthenone

1.6 cc. bromine.

The acenaphthenone was dissolved in 50 cc. carbon disulphide and the bromine dissolved in 25 cc. carbon disulphide was added gradually with shaking. After

a short time hydrogen bromide was copiously evolved. When the addition was complete, shaking was continued till the colour of bromine in the mixture disappeared. The carbon disulphide was then evaporated off and the product recrystallised from ligroin. Yield, 5.5 gm. (75% of theoretical). M.p., 111-112°. (Graebe and Jequier (loc. cit.) record 112°)

In another experiment, in which the solution of bromine in carbon disulphide was added all at once, no hydrogen bromide was at first evolved, and red crystals, presumably of an addition compound of bromine and acenaphthenone, separated. In a few minutes, particularly on shaking, the red compound decomposed rapidly with copious evolution of hydrogen bromide, the final solution being pale yellow in colour. On evaporating off the carbon disulphide and recrystallising from ligroin 1-bromo-acenaphthenone was obtained. Yield, 2.5 gm. from 2 gm. acenaphthenone (85% of theoretical) M.p., 111-112°.

Dibromination of acenaphthenone.

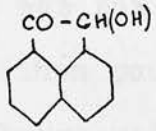
2 gm. acenaphthenone

2 cc. (approx. 3 mols.) bromine.

The acenaphthenone and the bromine were dissolved in 15 cc. and 40 cc. of carbon disulphide respectively. To the acenaphthenone solution 15 cc. of the bromine solution were added gradually with shaking in the cold, hydrogen bromide being evolved. After allowing

to stand for a short time, the solution was heated to the boiling point under reflux and the remainder of the bromine solution added gradually. After addition was complete boiling was continued till hydrogen bromide was no longer evolved. The carbon disulphide was evaporated off and the product recrystallised from ether when small almost white crystals, m.p. 161-162° were obtained. For 1:1-dibromo-acenaphthenone Berend and Herms (loc. cit.) record 160-161°.

Attempted Preparation of Acenaphthenonol.



(a)
(cf. Jenkins, J. Amer. Chem. Soc., 1934, 56, 682)

An alcoholic solution of sodium ethylate prepared from 0.34 gm. sodium was added to a solution of 1-bromo-acenaphthenone in the same solvent. On adding the first few cc. a reddish-yellow solid separated. Complete addition gave however a greenish-black solution, a slight greyish precipitate presumably of sodium bromide being also present. After standing for an hour the mixture was poured into 100 cc. of cold 15% hydrochloric acid, when an orange-coloured compound separated. This was filtered off, washed well with water, dried and recrystallised from nitro-benzene. Fine orange-red crystals of biacenaphthyl-idenedione, m.p. 300°, were obtained.

(b) 1-Bromo-acenaphthenone (2 gm.) was shaken for

6 hours with excess of freshly prepared moist silver oxide. The product on filtering, drying and extracting with ligroin gave a tarry substance from which a small amount of biacenaphthylidenedione, but no other recognisable product could be isolated.

Reduction of 4-Bromo-acenaphthenequinone.

4-Bromo-acenaphthenequinone (5 gm.) was heated in 100 cc. of boiling glacial acetic acid, and zinc dust (5 gm.) added gradually to the suspension. When addition was complete the mixture was boiled till a clear solution resulted. It was then poured into water and steam passed in. The large volume of distillate which was collected contained only a small quantity of a white product, melting at about 130°. On several recrystallisations from alcohol the melting point was raised to 172-4°, the yield being however very small. Since Mayer and Sieglitz (Ber., 1922, 55, 1835) record 174-5° as the melting point of 4-bromo-acenaphthenone, it may be assumed that this is the compound which has been at present obtained.

VI (C) The Nitration of Acenaphthenone.

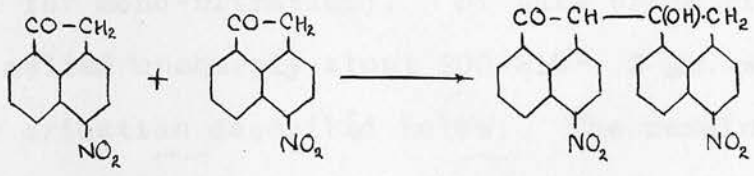
Since no record has been found in the literature of previous experiments on the nitration of acenaphthenone, this has been investigated in the course of the present work. By nitration in sulphuric acid solution with a mixture of nitric and sulphuric acids containing a molecular proportion of the former, a yellow crystalline compound melting with decomposition at 230° has been isolated. This was found to contain a percentage of nitrogen representing the calculated quantity for a mono-nitro-derivative of acenaphthenone. A striking property of the compound is its reaction with sodium hydroxide solution, in which it dissolves with the formation of a deep greenish blue colour. Acenaphthenone itself gives no similar reaction.

In this connection attention may be drawn to the behaviour of acenaphthenequinone and its substituted derivatives with sodium hydroxide solution. Whereas the quinone itself dissolves on boiling for a short time, 4-bromo-acenaphthenequinone and tribromo-acenaphthenequinone do not appear to react in this way. On the other hand 4-nitro- and 4:5-dinitro-acenaphthenequinones dissolve immediately in the cold, the solution in each case being deep brown in colour. In each case the original product can be recovered

by acidification.

The question of the position of the nitro-group in the new compound has been settled by oxidation. On treatment with sodium dichromate and glacial acetic acid a 60% yield of 4-nitro-naphthalic acid was obtained. The nitro-group is therefore present in the nucleus, occupying one of the peri-positions, the quite reasonable possibility that reaction would occur at the methylene group being eliminated.

It was not considered permissible however to assume that the compound is 4-nitro-acenaphthenone as it is hardly to be expected that this would have a melting point as high as 230°, the unsubstituted compound melting at 121°. There is present the possibility of the formation of complex condensation products. As a result of the positive inductive effect of the nitro-group on the methylene group it is plausible to assume that condensation of the aldol type $-\overset{|}{C}O + \overset{|}{C}H_2-\overset{|}{C}O \longrightarrow \overset{|}{C}(OH)-\overset{|}{C}H-\overset{|}{C}O$ will be facilitated. Thus in this particular case we might have:



Such a compound might be expected to dissolve in sodium hydroxide solution with a colour change such as has already been mentioned. Confirmation of a

bimolecular structure was not obtained however, attempts to determine the molecular weight by the ebullioscopic method using a differential thermometer as described by Menzies and Wright (J. Amer. Chem. Soc., 1921, 43, 2314) leading to no definite result.

Experimental

Nitration of Acenaphthenone.

3.4 gm. acenaphthenone

20 cc. concentrated sulphuric acid

Nitrating acid - 0.9 cc. nitric acid (d, 1.51) in 10 cc. concentrated sulphuric acid.

The acenaphthenone was dissolved in the sulphuric acid and the solution cooled in ice. The nitrating acid was dropped in gradually with constant shaking, the mixture being thereafter allowed to stand for three hours at room temperature. On pouring into water a yellow solid separated and after allowing to stand for some time this was filtered off, washed well with water and dried. Yield, 4.2 gm. (almost theoretical for mono-nitration). Of this crude product, which melted unsharply about 200-210°, 2 gm. were used in the oxidation described below. The remainder was extracted with ligroin, and the solution after separating from a dark brownish residue deposited on cooling crystals of a yellow substance, m.p. 215-220° (with decomposition). This product could be conveniently

recrystallised from a small volume of nitro-benzene, when yellow needles were obtained. On filtering, these were washed free from nitrobenzene, first with ligroin then with petrol ether (b.p. 40-60°). The melting point was found to be 230° on rapid heating. On slow heating melting was preceded by partial decomposition.

Analysis by micro-Dumas method.

Found: N, 6.61.

Calculated for $C_{12}H_7O_3N$: N, 6.57%.

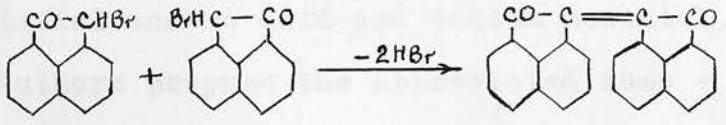
Oxidation of Nitration-product of Acenaphthenone.

The crude product (2 gm.) from the nitration described above was dissolved in 25 cc. glacial acetic acid by heating to 50°. Coarsely powdered dry sodium dichromate (10 gm.) was added gradually with stirring, the temperature in the ensuing reaction not being allowed to rise above 80°. The mixture was then heated on a boiling water-bath for three hours and thereafter poured into water acidified with sulphuric acid, when a yellow solid separated. After allowing to stand for a few hours this was filtered off, and washed with water. It was boiled with a solution of sodium carbonate (1 gm. in 200 cc. water) and filtered to remove a slight brownish residue. The filtrate was acidified with dilute hydrochloric acid when a yellowish precipitate was obtained. On filtering, washing with water and drying, this melted at 222-5°.

Yield, 1.4 gm. (60% of theoretical for nitro-naphthalic acid.) On recrystallising from glacial acetic acid the melting point was raised to 229-230°. Yield, 1 gm. A mixed melting point with an authentic specimen of 4-nitro-naphthalic anhydride (m.p. 230-231°) showed no depression.

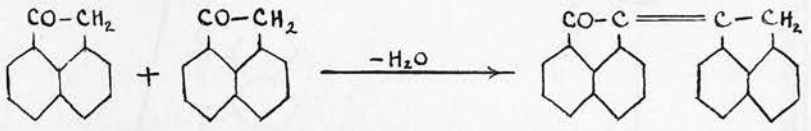
VII SOME OBSERVATIONS ON BIACENAPHTHYLIDENEDIONE.

Biacenaphthylidenedione was first obtained by Graebe and Gfeller (Ann., 1893, 276, 1) as a product of the controlled oxidation of acenaphthene, and also by the reduction of acenaphthenequinone by hydriodic acid and red phosphorus in a sealed tube at 115-125°. It was further obtained by Graebe and Jequier (Ann., 1896, 290, 195) on treating 1-bromoacenaphthenone with alkali.



Its preparation as a vat-dye has been claimed by the condensation of acenaphthenone and acenaphthenequinone (D.R.P., 212,858; C., 09, II, 775).

Graebe and Jequier (loc. cit.) obtained the related monoketonic compound - biacenaphthylidenone- by the condensation of two molecules of acenaphthenone when treated with alcoholic alkali or acetyl chloride



Biacenaphthylidenone also results from acenaphthylene dibromide on boiling in alcoholic solution with hydrochloric acid. The mechanism proposed is the intermediate formation of acenaphthylene-glycol and acenaphthenone (Dziewonski and Litynski, Ber., 1925, 58, 2539).

The parent hydrocarbon - biacenaphthylidene - from which these compounds are derived was prepared by Dolinski and Dziewonski (Ber., 1915, 48, 1917) by the polymerisation of acenaphthylene. It has also been obtained directly from the keto-compounds by Dziewonski and Litynski (loc. cit.) by reduction with zinc, glacial acetic acid and sodium acetate. The latter authors propose the abbreviated name - biacene - for the hydrocarbon. The keto-derivatives are then termed biacendione and biacenone respectively. This nomenclature will not however be adopted here, since not being rational its only advantage is brevity.

The various reactions which have been mentioned

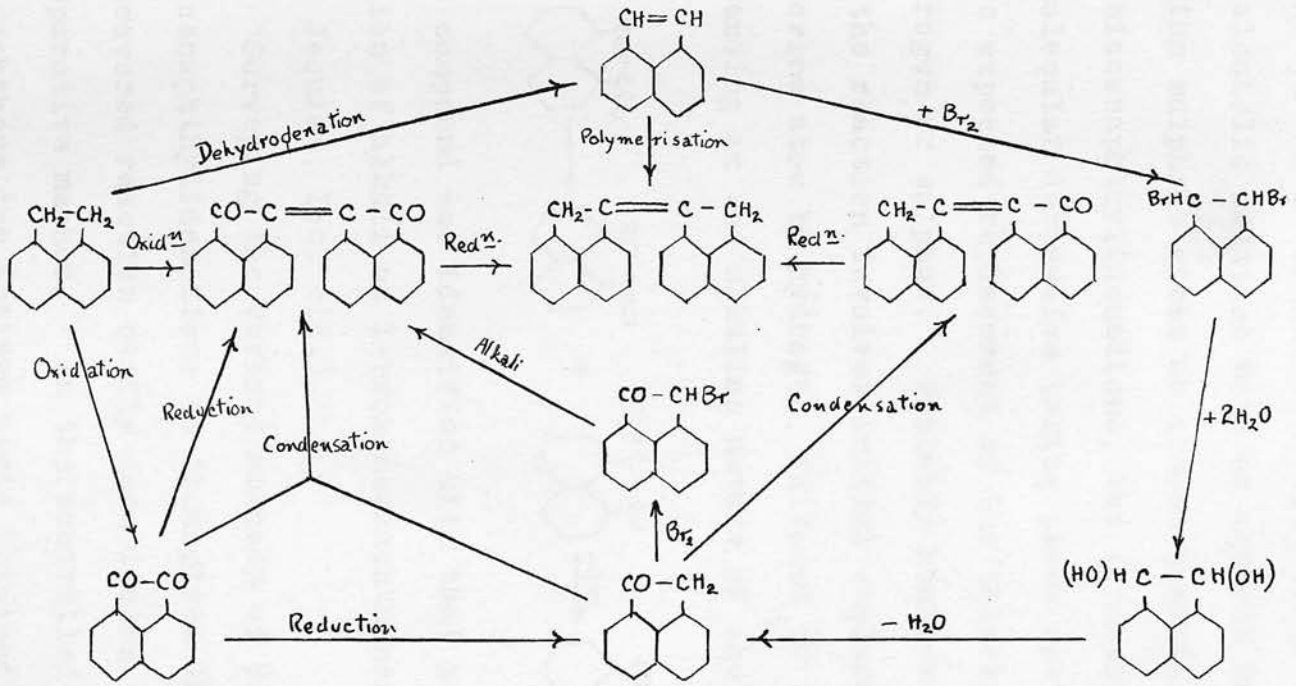
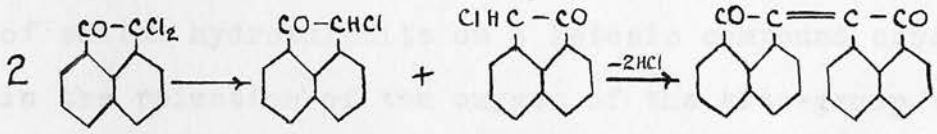


Diagram showing the Synthetic Relationships between Compounds of the Acenaphthene Group and Bimolecular Derivatives

above are represented diagrammatically on p.131.

In the course of the present work it has been found that 1:1'-dichloroacenaphthenone when treated in alcoholic solution with an aqueous solution of sodium sulphide gives an almost quantitative yield of biacenaphthylidenedione, the formation of this bimolecular derivative taking place instead of the more expected replacement of the chlorine atoms by hydrogen or sulphur. Probably however the mechanism of the reaction involves initial replacement of a chlorine atom by hydrogen, followed by condensation depending on the alkaline nature of the medium.

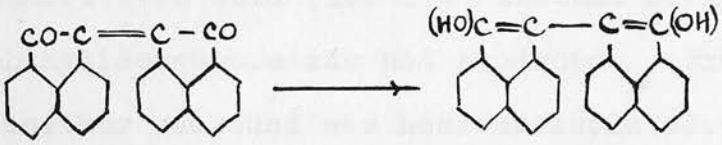


The compound was identified with that produced by the action of alkali on 1-bromoacenaphthenone. (Graebe and Jequier, loc. cit.)

Surveying the various methods of preparing biacenaphthylidenedione it transpires that the newly discovered reaction easily constitutes the best preparative method. In the controlled oxidation of acenaphthene the optimum yield obtained has been 10%, whereas the reduction of acenaphthenequinone in a sealed tube with red phosphorus and hydriodic acid is inconvenient and limited to small quantities. Preparation from 1-bromoacenaphthenone is limited by the somewhat

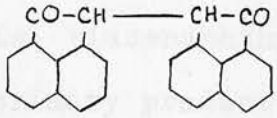
inaccessible nature of this compound.

When a test was made of the dyeing properties of biacenaphthylidenedione it was found that it could not be vatted under the usual circumstances with sodium hydrosulphite in alkaline solution. Instead of a coloured vat a white insoluble compound was formed. The nature of this compound, which was not readily oxidised back to biacenaphthylidenedione, being quite unchanged even after long exposure to air, was investigated. It was found that a pure white compound (m.p. 258°) could be obtained by recrystallisation from nitrobenzene. It was not acetylated on boiling with acetic anhydride. The usual action of sodium hydrosulphite on a ketonic compound consists in the reduction of the oxygen of the keto-group to a hydroxyl group, the properties of vat-dyes depending on the solubility of the resulting product. In the present case a priori we might expect the following reduction:-



Vatting does not occur however under the usual circumstances and the compound above obtained could not be acetylated. It seemed plausible to consider the compound as being an isomeride of the above (hypothetical) hydroxy-compound, reduction taking place

at the double bond or possibly keto-enolic tautomerism being present, the keto form only being stable.



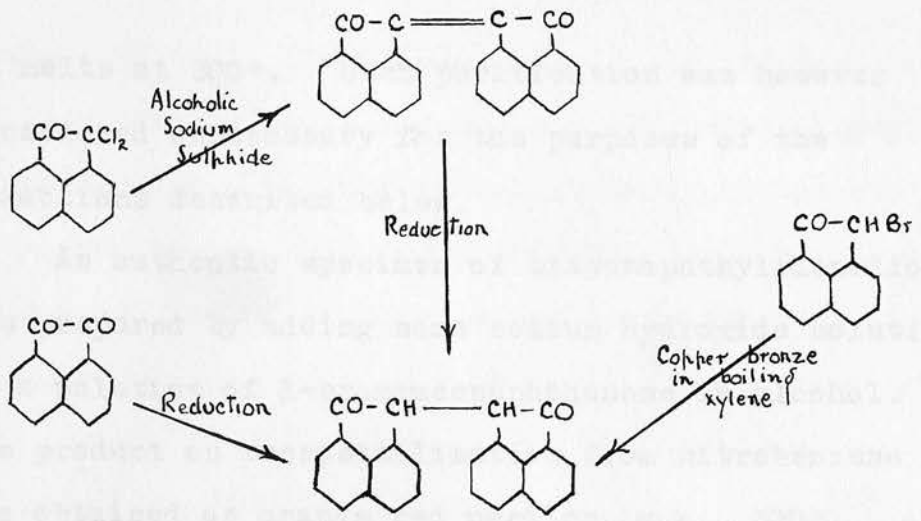
A compound of this structure would be called 1:1'-diacenaphthenonyl. The same compound was obtained by the careful reduction of biacenaphthylidenedione with zinc dust or iron filings and glacial acetic acid. Its properties and direct comparison showed it to be quite different from either biacenaphthylidenone or biacenaphthylidene. (II and III in diagrams on p.131)

In the course of the work on these compounds occasion was found to repeat the reduction of acenaphthenequinone with red phosphorus and hydriodic acid, cf., Graebe and Gfeller (loc. cit.). It was observed that, when temperatures higher than those given by these authors were used (160-170° instead of 115-125°), biacenaphthylidenedione was not produced. From the product another compound was however isolated. This was considered of particular interest as Graebe and Gfeller record unsuccessful attempts to obtain compounds other than biacenaphthylidenedione by this method of reduction. When quite pure the new compound obtained was white and melted at 258°; a mixed melting point showed it to be identical with the compound which has just been described as being obtained

from biacenaphthylidenedione by reduction with sodium hydrosulphite, or iron and acetic acid. This second method of obtaining the compound may be regarded as similar in principle, biacenaphthylidenedione being considered as the primary product, further reduction of which gives the new compound.

A decisive method of proving the structure suggested above, namely that the new compound is 1:1'-diacenaphthenonyl, has been evolved. It was considered that if condensation could be made to take place between two molecules of 1-bromoacenaphthenone with loss of bromine only, a compound having the structure in question would be synthesised.

This reaction has been found to take place with copper bronze in boiling o-xylene. The resulting compound was found to be identical with that obtained by the various reduction methods described above. The various new reactions and relationships now established may therefore be represented diagrammatically as below, and correlated with those in the diagram on p.131, which summarises the work of a number of previous investigators.



Experimental

Preparation of Biacenaphthylidenedione.

10 gm. 1:1'-dichloroacenaphthenone (for preparation see p.104)

12 gm. sodium sulphide crystals ($Na_2S.9H_2O$)

The dichlorocompound was dissolved in 200 cc. 95% alcohol, and to the boiling solution the sodium sulphide, dissolved in 50 cc. water, was added fairly rapidly. Vigorous reaction took place immediately with precipitation of the product. The mixture was maintained for a short time at the boiling point care being taken to avoid excessive bumping. The orange-red flocculent precipitate of biacenaphthylidenedione was filtered off from the hot solution, washed with a little warm alcohol, then with hot water. After a final washing with alcohol and a little ether the product was dried. Yield, 6.5 gm. (93% of theoretical) M.p. 295-7°. The compound can be purified by recrystallisation without much loss from nitrobenzene, when

it melts at 300°. Such purification was however considered unnecessary for the purposes of the reductions described below.

An authentic specimen of biacenaphthylidenedione was prepared by adding some sodium hydroxide solution to a solution of 1-bromoacenaphthenone in alcohol. The product on recrystallisation from nitrobenzene was obtained as orange red needles, m.p., 300°. A mixed melting point with the compound obtained above was not depressed. Moreover the characteristic deep green colouration with concentrated sulphuric acid, which changes to red on addition of a drop of concentrated nitric acid, was obtained.

Reductions of Biacenaphthylidenedione.

A. 2 gm. biacenaphthylidenedione
2 gm. sodium hydrosulphite.

The keto-compound was suspended in a mixture of 75 cc. water and 25 cc. bench sodium hydroxide solution (10%). The hydrosulphite was added and the temperature of the mixture raised to the boiling point. Gradually the orange-red colour of the biacenaphthylidenedione disappeared, a suspension of a white compound being obtained. The latter was filtered off, washed with water, and dried. Yield, 1.9 gm. M.p. 250-255°. On recrystallisation from nitrobenzene white needles were obtained, m.p. 258°.

Yield, 1.2 gm. The compound could also be recrystallised from glacial acetic acid or acetic anhydride. In neither case was any change observed in the product even on prolonged boiling, indication of the absence of hydroxyl groups being thus obtained.

B. Biacenaphthylidendione (2 gm.) was dissolved in 100 cc. glacial acetic acid. Iron filings (2 gm.) were added gradually to the boiling solution, and when addition was complete the mixture was boiled till the orange-red colour of the biacenaphthylidenedione disappeared. The product was soluble in the acetic acid used, and the hot solution was filtered and allowed to crystallise. Long needles were obtained, m.p. 250-253°. On recrystallisation from glacial acetic acid the melting-point was raised to 256-258°. A final recrystallisation from nitrobenzene gave fine white needles of m.p. 259°, the product being identical with that obtained by reduction with sodium hydrosulphite in alkaline solution.

In the above reduction zinc dust could be used instead of iron filings.

Reduction of Acenaphthenequinone.

(Modification of conditions used by Graebe and Gfeller (Ann., 1896, 276, 1) leading to a different product)

3 gm. acenaphthenequinone

0.3 gm. red phosphorus

25 cc. approx. 17% hydriodic acid.

The red phosphorus and acenaphthenequinone were intimately mixed and introduced into a Carius tube containing the hydriodic acid. The tube was sealed and heated for five hours at 160-170°. At the end of that time the contents of the tube did not present the appearance reported by Graebe and Gfeller when a temperature of 115-125° was used. The product instead of being red in colour was almost black. It was filtered off, washed well with water, dried and recrystallised from nitrobenzene (10 cc.). A crystalline compound separated from the dark-coloured nitrobenzene solution. On filtering and washing first with cold nitrobenzene and then with alcohol, fine white needles were obtained. Yield, 1.2 gm. (44% of theoretical for 1:1'-diacenaphthenonyl) M.p., 258°.

Analysis.

Found: C, 86.06; H, 4.08.

Calculated for $C_{24}H_{14}O_2$; C, 86.24; H, 4.19%.

The above experiment could be repeated with the same result. The identity of the product with that already obtained by reduction of biacenaphthylidenedione was established by a mixed melting point determination, no depression being observed.

Preparation of 1:1'-diacenaphthenonyl.

1.2 gm. 1-bromo-acenaphthenone

10 cc. o-xylene

0.6 gm. copper bronze.

The copper bronze was added fairly rapidly to a boiling solution of the bromo-compound in the xylene. The mixture was kept gently boiling for one hour and filtered while hot from excess copper and from the cuprous bromide formed. On allowing the filtrate to cool crystallisation occurred and fine, white needles of a product of melting point 246-8° were obtained (0.2 gm.). Recrystallisation from nitrobenzene raised the melting point to 255-6°. Another recrystallisation, from acetic acid in which the compound is more sparingly soluble, raised the figure to 258°. A mixed melting point proved the identity of the product with the compound obtained by the reductions described above, and hence the constitution of the latter.

SUMMARY

I Acenaphthenequinone has been mono-brominated and the product shown to be 4-bromo-acenaphthenequinone, the direct bromination described being the best method of preparing the latter compound. Various derivatives, have been prepared, including 4-bromo-naphthalic anhydride by oxidation with hydrogen peroxide in alkaline solution.

II The bromination of naphthalic anhydride has been studied. The product obtained by the action of bromine in a mixture of oleum and concentrated sulphuric acid has been shown to be 3-bromo-naphthalic anhydride and not the 4-bromo-derivative as has hitherto been assumed. It has been shown that 3-sulpho-naphthalic anhydride is not formed as an intermediate stage in this reaction. The same compound was obtained by the action of bromine on naphthalic anhydride in a sealed tube, and an improved method of preparing it, namely by the action of bromine in concentrated nitric acid, is described.

Proof of the constitution of the 3-bromo-naphthalic

anhydride consisted in a direct comparison with a specimen prepared from 3-nitro-naphthalic acid by reduction, diazotisation and treatment with cuprous bromide. Further confirmation follows from the work on the mercuration summarised below.

On the other hand, by the bromination of naphthalic acid (as alkali salt) by bromine in presence of alkali hypobromite, 4-bromo-naphthalic anhydride has been prepared.

Derivatives of the two mono-bromo-naphthalic anhydrides have been prepared for purposes of comparison.

III Mercurations of 3-bromo- and 4-bromo-naphthalic anhydride have been carried out. From the mixture obtained by hydrolysis of the mercuration product from the former, the hitherto unknown 3-bromo-naphthoic acid was obtained, its constitution being proved by direct comparison with a specimen prepared from 3-nitro-naphthoic acid by reduction, diazotisation and treatment with cuprous bromide. Hydrolysis of the mercuration product from 4-bromo-naphthalic anhydride gave a mixture from which 5-bromo-naphthoic acid was isolated. This compound is already described in the literature, being prepared by the bromination of naphthoic acid. Identity of specimens from the two sources was proved.

IV (a) The introduction of more than one atom of

bromine into acenaphthenequinone and naphthalic anhydride respectively has been studied. In each case a tribromo-derivative has been obtained, the orientation of the bromine atoms being the same, since the tribromo-acenaphthenequinone on oxidation gave a tribromo-naphthalic anhydride identical with that obtained directly from naphthalic anhydride. It has not yet been possible decisively to prove the positions of the bromine atoms.

(b) The mono-nitration of 4-nitro-naphthalic anhydride (obtained by oxidation of 4-nitro-acenaphthene) has been shown to give 4:5-dinitro-naphthalic anhydride.

On the other hand when 4-bromo-naphthalic anhydride is nitrated it yields 3-nitro-4-bromo-naphthalic anhydride. To prove the constitution of the latter compound it was synthesised in a manner showing its constitution, being prepared by the oxidation of 3-nitro-4-bromo-acenaphthene, which was obtained from the already known 3-nitro-4-amino-acenaphthene by diazotisation and treatment with cuprous bromide.

V The condensation of naphthalic anhydride and its substituted derivatives with o-phenylenediamine has been shown to take place in glacial acetic acid with loss of two molecules of water to give 1:8-naphthoylene-1:2-benziminazole and its derivatives. When the naphthalic anhydride was of a symmetrical

structure, a well-defined derivative was obtained, but unsymmetrical anhydrides gave mixtures of compounds which could not be separated.

VI (a) A study has been made of methods for the preparation of acenaphthenone, some new methods being described. The best preparative method was found to be the reduction of acenaphthenequinone oxime, which can be prepared directly from acenaphthene. Reduction of acenaphthenequinone phenylhydrazone also provides a serviceable method.

In connection with this work the preparation of acenaphthenequinone anil, Wolff's reaction on acenaphthenequinone semicarbazone, the action of ammonia on 1:1-dichloro-acenaphthenone and that of methylamine on acenaphthenequinone have been investigated. The imide and methylimide expected in the last two cases respectively were not obtained, condensation between two molecules taking place to form azine derivatives.

(b) Acenaphthenone on direct bromination yields first 1-bromo-acenaphthenone and on further bromination 1:1-dibromo-acenaphthenone. Attempts to evolve indirect preparative methods for bromo-derivatives of acenaphthenone substituted in the nucleus were not successful.

(c) By nitration of acenaphthenone a compound has been obtained which on oxidation yields 4-nitro-

naphthalic anhydride. A definite conclusion with regard to its constitution has not however been reached.

VII A new method is described for the preparation of biacenaphthylidenedione, this compound resulting quantitatively by the action of sodium sulphide on 1:1-dichloro-acenaphthenone in alcoholic solution. By reduction of biacenaphthylidenedione with sodium hydrosulphite in alkaline solution, or with iron filings and glacial acetic acid, a new compound, which also results from the reduction of acenaphthene-quinone with hydriodic acid and red phosphorus at 160-170° has been obtained. It has been proved to be 1:1'-diacenaphthenonyl by synthesis of the latter by a method showing its constitution, namely by the action of copper bronze in boiling xylene on 1-bromo-acenaphthenone.

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